Cyclopropanes. XXVI. Electrolytic Reduction of Optically Active 1-Halo-1-methyl-2,2-diphenylcyclopropanes[1]

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Abstract: The electrochemical reduction of optically active 1-halo-1-methyl-2,2-diphenylcyclopropanes has been investigated using cyclic voltammetry, controlled potential electrolysis and stereochemical techniques. The cyclic voltammetry curves showed three well-defined peaks for all halides examined. The nature and significance of these peaks is discussed. The controlled potential electrolyses of the halides at a mercury electrode produced complex current-time relationships which are attributed to the formation of organomercurials. Reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane, 1-iodo-1-methyl-2,2-diphenylcyclopropane, and 1-methyl-2,2-diphenylcyclopropylmercuric bromide lead to 63, 53, and 100% retention of configuration, respectively.

The electrochemical reduction of the carbon–halogen bond has been studied for three decades. However, the mechanism of this reaction had been probed very little until recent years. Among the earliest reports of carbon–halogen reduction were those of Plump and Hammett[3] and of von Halban and coworkers,[4] but the first systematic investigation was reported by von Stackelberg and Stracke,[5] who proposed the reaction scheme shown in eq 1.

$$\mathrm{RX} \xrightarrow{+e^-} \mathrm{R}\cdot + \mathrm{X}^- \xrightarrow{+e^-} \mathrm{R}^- \xrightarrow{\mathrm{SH}} \mathrm{RH} + \mathrm{S}^- \qquad (1)$$

Elving and coworkers[6] performed an extensive investigation of carbon–halogen bond fission, on the basis of which they proposed electrochemical mechanisms analogous to nucleophilic substitution reactions, with the cathode as nucleophile. There have been several attempts to draw conclusions about these mechanisms from correlations of changes in polarographic halfwave potentials with changes in structure,[7] however, it has been concluded that the available evidence does not support the concept of an analogous relationship between electrochemical and homogeneous nucleophilic reactions.

The preliminary report of the present work[8] was the first study of the stereochemistry of an electrochemical reduction of a carbon–halogen bond. The reduction of the optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane led to 63% retention of configuration and it was suggested that radicals, carbanions, and organomercurials were intermediates in the reduction. Several papers dealing with the stereochemistry of electrolytic halide reduction have, subsequently, appeared.[9]

Work in this laboratory has been concerned with the interaction of organic halides and metals for a number of years.[10] These investigations eventually led to the development of a physicochemical tool for studying the mechanism of such reaction. This tool is the stereochemical behavior of the optically active 1-halo-1-methyl-2,2-diphenylcyclopropanes. The cyclopropyl system is ideally suited for the investigation of the mechanism of electrolytic reduction of carbon–halogen bonds, since the optical purities and absolute configurations of both the starting materials and the product, 1-methyl-2,2-diphenylcyclopropane, are known.[11]

Moreover, in contrast to most other tertiary halides, this system is unique in that it is relatively stable toward SN1 solvolysis thus permitting us to remove from consideration the incursion of a cationic intermediate.[12] Finally, the optical fate of the 1-methyl-2,2-diphenylcyclopropyl radical[13] as well as the carbanion[14] has been established, the radical leading to complete racemization and the carbanion to almost complete retention of optical activity and configuration. Other workers[9a,15] have concurred in the usefulness of this system for stereochemical studies.

Results

In the work to be described, experiments were performed on a variety of cyclopropane derivatives which will be designated as follows: 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**), RBr; 1-iodo-1-methyl-2,2-diphenylcyclopropane (**2**), RI; bis(1-methyl-2,2-diphenylcyclopropyl)mercury (**3**), R_2Hg; 1-methyl-2,2-

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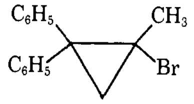
diphenylcyclopropylmercuric bromide (**4**), RHgBr. Other compounds of interest are 1-bromo-2,2-diphenylcyclopropane (**5**) and 1-bromo-1-methoxymethyl-2,2-diphenylcyclopropane (**6**).



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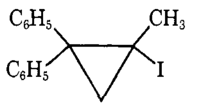

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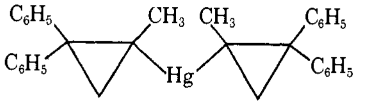

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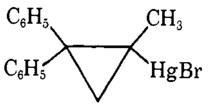

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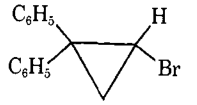

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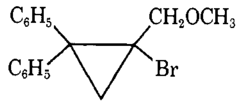

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Cyclic Voltammetry. The reactions of the compounds studied were observed by cyclic voltammetry at a mercury electrode. Using sweep rates of about 10 V/sec, monobromo and iodo compounds showed one irreversible cathodic peak which corresponds to the wave observed by dc polarography. In the discussion this will be designated the "A" peak. From the listing of peak potentials in Table I, it is seen that the A peaks occur in the range from -2.2 to -3.0 V *vs.* Ag–AgNO$_3$.

Table I. Cyclic Voltammetric Peak Potentials[a] *vs.* Ag–AgNO$_3$ (0.10 *M*)

Compound	Peak A	Peak B	Peak C
1-Bromo-1-methyl-2,2-diphenylcyclopropane (**1**)	-3.00	-1.26	-1.58
1-Iodo-1-methyl-2,2-diphenylcyclopropane (**2**)	-2.28	-1.26	-1.58
1-Bromo-2,2-diphenylcyclopropane (**5**)	-2.97	-1.31	-1.69
1-Bromo-1-methoxymethyl-2,2-diphenylcyclopropane (**6**)	-2.95	-1.43	-1.79
1-Methyl-2,2-diphenylcyclopropylmercuric bromide (**4**)	-2.57	-0.62	-1.22
1,2-Dibromoethane	-2.22		

[a] Measured at a mercury-plated platinum microelectrode at 10 V/sec sweep rate. Concentration of reactants was ~5 m*M* in 0.1 *M* Et$_4$NBr–MeCN at ~22°.

As the microelectrode potential is cycled in the positive direction after observation of the A peak, an anodic peak, designated the "B" peak, appears at around -1.3 V. If the potential scan is again reversed after occurrence of the B peak, a second cathodic peak is seen around -1.6 V. This will be termed the "C" peak. Typical voltammograms have been published.[8]

Voltammetric behavior indicates that the B and C peaks are caused by reactions of products of the A reaction. Several observations support this conclusion. If the microelectrode potential is swept from an anodic rest point to observe the A peak, then reversed and swept back to the rest point, only the A and B peaks are seen, indicating that products from the A and/or B reactions must be present before the C reaction takes place.

If the potential is continuously cycled over the region in which all peaks can be observed, and the solution is then stirred, the A peak height is increased, compared to its value with a still solution; at the same time, the B and C peaks are decreased. This would be expected if the A peak reactant were coming from the bulk of the solution, but the B–C peak reactants were produced at the electrode. If, during continuous cycling of the potential, the range is restricted from the negative extreme to exclude the A peak, the B–C peaks disappear after a few seconds, even though the electrode potential is being scanned through the region in which they occur. If the sweep limits are again extended to include the A peak, the B–C peaks can then be observed.

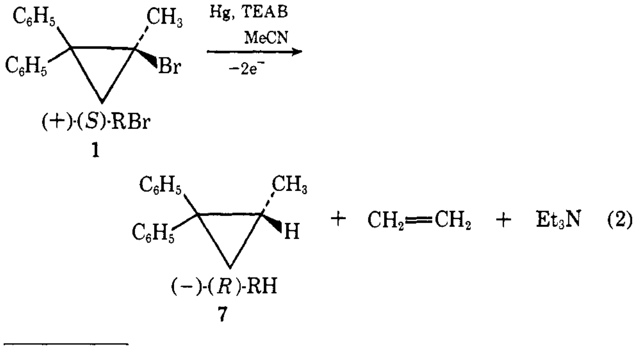
Proton donors such as phenol, methanol, ethanol, *n*-hexanol, and 2,2,2,3-tetrafluoropropanol-1 prevent the B peak from being observed and also eliminate the C peak, without altering the A peak in any way, in agreement with the results reported by Petrovich and Baizer.[16]

The dialkylmercury R$_2$Hg (**3**) is, as expected, not reduced at a mercury electrode and addition of triethylamine did not change this. However, the alkyl mercuric bromide, RHgBr (**4**) showed a quasireversible reduction step ("B–C" peaks) at about -1.0 V and an irreversible step at -2.6 V (A peak). In contrast to the behavior of RBr and RI, the B–C peaks of RHgBr are the result of a direct reduction of the substrate; prior occurrence of the A reaction is not necessary for them to be observed.

When the voltammogram of a mixture of RBr and RHgBr is recorded, the A peaks of each compound are observed; however, only the B–C peaks for RHgBr are seen. When RHgBr is added to a solution of RBr, the B–C peaks of RBr are observed to disappear and be replaced by those for RHgBr at a different potential. This indicates that neither of the familiar mercury compounds, R$_2$Hg or RHgBr, is responsible for the B–C peaks observed with RBr.

The possibility that a solvent fragment might be responsible for the B–C peaks of RBr was considered; however, voltammetric behavior in N,N-dimethylformamide (DMF) and in dimethoxyethane was qualitatively similar to that in acetonitrile. Accordingly, direct involvement of the solvent appears unlikely. One difference was noted when RBr was reduced in tetraalkylammonium perchlorate–DMF mixtures; the A peak appeared to be somewhat reversible.

Controlled Potential Electrolysis. Controlled potential reduction of RBr or of (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane, produced the corresponding hydrocarbon, 1-methyl-2,2-diphenylcyclopropane (**7**), RH. In addition, as indicated in eq 2,



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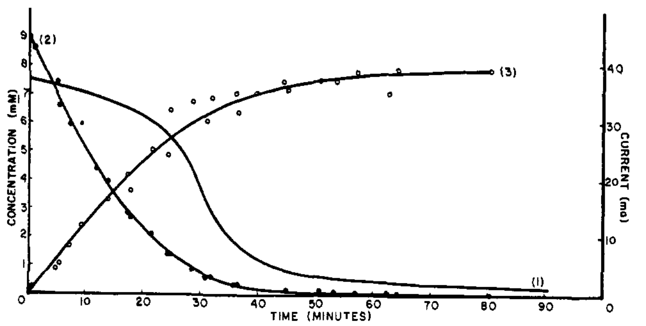


Figure 1. Curve 1, electrolysis current *vs.* time; curve 2, concentration of RBr (**1**) *vs.* time; curve 3, concentration of RH *vs.* time.

ethylene and triethylamine, derived from the tetraethylammonium bromide (TEAB) supporting electrolyte, were products of the reaction. Reduction of RBr at a mercury electrode required 2.0 electrons per molecule and occurred with a net retention of configuration to yield 25% optically pure RH. Data are presented in Table II. Reduction at a carbon electrode yielded RH with 46.8% optical purity. The addition of phenol to the reaction had no effect on the optical purity of RH, in contrast to its effect on the cyclic voltammetry curves mentioned earlier.

Table II. Controlled Potential Reduction of (+)-(*S*)-RBr in Acetonitrile[a]

Yield of[b] RH (**7**), mole %	*n*[g]	Optical purity[c] of **7**, %	Remarks
89.0		25.5	
87.3		25.8	
41.5	2.04	24.1	Low yield due to mechanical loss
74.2	2.43	46.8	Glassy carbon cathode
77.0	2.25	22.9	Added 1.76 moles of phenol per mole of RBr
79.2	1.90	21.0	Added 5.35 moles of phenol per mole of RBr
82.0	2.30	24.2[d]	CD_3CN used as solvent; gave RH with 75% D in position 1[e]
		13.5	Reaction was stopped after approximately 50% completion[f]

[a] Reduction of approximately 100-μmole quantities of RBr at −2.9 V *vs.* Ag–0.10 *M* $AgNO_3$ reference in 0.10 *M* TEAB-MeCN; mercury pool cathode except where noted. [b] Actual recovery, analyses of product mixtures showed 99% conversion of RBr to RH. [c] Retention of configuration in all cases. [d] Calculated on the basis of $[\alpha]_{Hg}$(max) for RH. [e] D content determined by nmr and mass spectrometry. [f] Recovered RBr optically pure. [g] Integrated current, faradays per mole of RBr.

The recovery of triethylamine and ethylene from the reaction mixture suggested that the supporting electrolyte, TEAB, had been cleaved by the attack of a strong base on the β protons of the ethyl groups in TEAB. This base could have been the carbanion derived from the alkyl halide *via* a two-electron reduction or an anion produced by the alkyl carbanion reacting with the solvent. Therefore, the amounts of these materials were determined; results are summarized in Table III.

Table III. Glpc Analysis of Triethylamine and Ethylene Formed during the Reduction of RBr (**1**) in Acetonitrile–TEAB[b]

RBr, μmole	*n*	% C_2H_4[a]	% Et_3N[a]	% H_2O[c]
108	1.95	80		
100	1.95	42		
108	1.97	94		
108	2.14	18	17	
112	1.92	47		
51	2.00	20	44	33
103	2.05	41	0	105
103	2.14	28		53
69		44		2100

[a] The sum of the amounts found in the cathode solution, cathode head space, anode solution, and anode head space, mole per cent of RBr taken. [b] All reductions were carried out at a mercury pool cathode and at −2.90 V *vs.* Ag/Ag$^+$ (0.1 *M*). [c] Based on μmoles of RBr.

Carrying out the reduction of RBr in CD_3CN produced hydrocarbon that contained 75% deuterium in position 1. This shows that the major source of hydrogen in the product is the solvent, rather than the supporting electrolyte. The average yield of ethylene was 46%. Therefore, a major portion of it was produced by the cleavage of TEAB by a secondary anion, probably [CH_2CN^-]. To ascertain the effect of water on the formation of ethylene, experiments described in Table III in which the water concentration was less than, equal to, and much larger than that of starting RBr were performed. They show clearly that water neither promotes nor inhibits the production of ethylene. The erratic yields of ethylene are rather surprising and have not been rationalized. Triethylamine was distilled from the reaction mixture and identified as its picrate. It was also detected by glpc. Examination of the reaction mixture by glpc also revealed a small amount of methane, but repeatedly failed to detect even a trace of succinonitrile.

The reduction of RBr was carried out in other solvent-electrolyte systems; the resulting data are summarized in Table IV. These data reveal an iodide ion effect. The optical purity of RH drops from the usual range of 21–25% to 6–10% when iodide is present in the reaction mixture. Changing the solvent from acetonitrile to DMF or ethylenediamine had no effect if a perchlorate salt was used as the supporting electrolyte. However, dimethoxyethane gave total racemization even in the presence of perchlorate salts. The addition of phenol to the reactions run in DMF had no effect on the optical purity of hydrocarbon, regardless of the nature of the electrolyte anion.

Current–Time Relationship. If the variation of reaction current with time is measured during a constant potential electrolysis, a first-order exponential decay of current will be observed when the reaction is not subject to mechanistic complications. This is the case in the present work when RBr is reduced at a glassy carbon electrode or when RHgBr is reduced at a mercury electrode. The behavior observed during reduction of RBr at a mercury electrode is illustrated in Figure 1. Here reaction current, concentration of RBr, and concentration of RH produced are plotted on the same time scale. It is seen that while the starting compound does show an approximately exponential decay with time, the reaction current decreases much less rapidly during the early part of the experiment. Since an *I-T* curve of this shape could be caused by limiting of the potentiostat or by uncompensated ohmic drop between the

Table IV. Controlled Potential Reduction of RBr (**1**) in Various Solvent Systems[a]

Solvent	Electrolyte	Reaction potential V *vs.* sce	RBr taken, μmole	Mole % RH isolated	*n*	% optical purity of RH	Remarks
DMF[b]	TBAI[c]	−2.50	108.0	71.6	1.92	6.8	1% $Ph_2C{=}CMe_2$ and 2.6% **8** formed
DMF	TBAI	−2.50	108.2	75.5	2.16	8.6	0.2 mmole of phenol added
DMF	TBAI	−2.50	51.4	74.8	2.72	9.7	0.2 mmole of phenol added
DMF	TBAI	−2.60	119.5	91.2	2.06	6.6	0.2 mmole of phenol added
DMF	TPAP[d]	−2.50	57.1	91.9	1.98	24.2	1.9% **8** formed
DMF	TPAP	−2.50	57.1	91.5	2.16	25.4	0.1 mmole of phenol added
EDA[e]	TEAB	−2.00	69.5	87.5	1.60	5.0	6.1% **8** formed
EDA	TBAI	−3.00	90.6	85.2		20.4	
DME[f]	TBAP[g]	−3.40[h]	54.6	62.0	2.03	0.0	
DME	TBAP	−3.24[h]	54.6	71.0	3.43	0.0	

[a] Mercury electrode in all cases. [b] N,N-Dimethylformamide. [c] Tetra-*n*-butylammonium iodide. [d] Tetra-*n*-propylammonium perchlorate. [e] Ethylenediamine. [f] Dimethoxyethane. [g] Tetra-*n*-butylammonium perchlorate. [h] Ag–0.10 *M* $AgNO_3$ reference electrode.

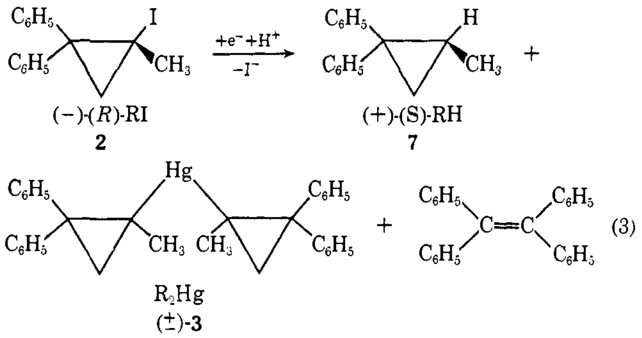
reference and working electrodes, these factors were carefully considered.

In all experiments, electrolysis current and total cell voltage drop were well within the capabilities of the potentiostat. The reference probe tip was kept 2–15 mm from the cathode pool. Maximum electrolysis current was usually less than 30 mA and one run was made with a maximum current of 5 mA to assure that uncompensated resistance drop would be small. In all cases, the *I–T* curve had the shape illustrated in Figure 1. In other work, we have observed unusual *I–T* curves which were affected by resistance-drop artifacts.[17] In these cases, the substrate concentration–time curves had the same shape as the *I–T* curves. Ethyl bromide, cyclopropyl bromide, RI (**2**), and isopropyl iodide gave *I–T* curves qualitatively similar to those observed for RBr.

Examination of the data in Figure 1 shows that during the early part of the experiment, RBr disappeared more rapidly than RH was being formed. RBr was not being converted directly into RH, but instead an intermediate was involved. The intermediate was thought to be an organomercurial and supporting evidence was obtained by removing samples from the reaction during the reduction. These samples were analyzed colorimetrically for mercury by wet oxidation and subsequent dithizone color formation. A solution containing 126.4 μmoles of RBr was electrolyzed. Samples were taken when one-third the expected number of coulombs had passed and when the reaction was complete. On analysis of these samples and a blank similarly electrolyzed, no detectable mercury (<0.1 μg/ml) was found in either the final sample or the blank. The intermediate sample contained 1.6 μmoles of mercury (45 μg/ml) which corresponds to 1.27 μmoles of mercury/100 μmoles of RBr.

An attempt was made to detect the organomercurial intermediate by tlc during the reduction of RBr. However, this revealed only decreasing amounts of RBr and increasing amounts of RH. The same experiment was interrupted after approximately 50% of the required current had passed and subsequently subjected to preparative tlc. (The concentration of the organomercurial would still be near its maximum at the point of interruption.) Analysis of the various bands from the tlc plate by atomic fluorescence[18] revealed that all the mercury present remained at the origin when the plate was developed with *n*-hexane. Development with a mixture of 20% methanol–80% chloroform moved the mercury about half way up the plate. This suggests an organomercurial or at least mercuric bromide, rather than mercury metal. Either of the former could have arisen from decomposition of an original organomercurial intermediate. The concentration of mercury in the crude reaction mixture was determined to be 105 μg/ml, equivalent to 0.01 mole of mercury for each mole of alkyl bromide taken originally.

1-Iodo-1-methyl-2,2-diphenylcyclopropane (**2**), RI, gave a cyclic voltammetry curve very similar to that of its bromo analog. However, the controlled potential electrolysis results are different in several respects. The formation of R_2Hg in eq 3 illustrates one of these differences. (−)-(*R*)-RI (**2**) yielded (+)-(*S*)-RH (**7**),



which corresponds to retention of configuration, as in the reduction of RBr.

The electrochemical conversion of RI into R_2Hg requires 1 F/mole while the transformation of RI to RH requires 2 F/mole. Therefore, the value of *n* for the reaction shown in eq 3 should be between 1 and 2 depending upon the amount of R_2Hg formed. The relationship between yields of RH and R_2Hg was studied as a function of potential and the results are summarized in Table V. The observations in Table V were corroborated in preparative controlled potential electrolysis experiments at high and low control potentials.

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(17) Using the same equipment and under identical conditions RHgBr gave a normal curve. Moreover, when a carbon electrode was used to reduce RBr, rather than the mercury electrode, again a normal curve was observed.

(18) We are indebted to Dr. T. J. Vickers for the atomic fluorescence analyses.

Table V. Variation in Yield of R_2Hg with Potential on Reduction of RI[a]

Reaction potential V *vs.* Ag-AgNO$_3$	*n*	% conversion of RI to R_2Hg[b]
−2.10	1.32	39.9
−2.17	1.37	
−2.37	1.53	
−2.47	1.57	
−2.50	1.62	29.9
−2.90	1.75	18.9

[a] Reaction at a mercury pool cathode. [b] Calculated from the mercury analysis by wet oxidation and colorimetric determination by dithizone method.

Table VI. Controlled Potential Electrolysis of RI in Acetonitrile–TEAB at a Mercury Cathode

Reaction potential V *vs.* Ag-AgNO$_3$	% RH isolated[a]	% optical purity of RH[b]	% R_2Hg isolated[a]	% optical purity of R_2Hg
−2.16	53.9	3.9	44.0	0
−2.80	75.4	3.2	16.8	0

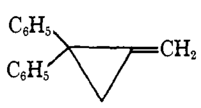
[a] Mole per cent of RI taken. [b] Retention of configuration.

Results are given in Table VI. In these experiments the ratio of hydrocarbon and dialkylmercury changed from 1.22 at a reduction potential of −2.16 V to 4.50 at a potential of −2.80 V.

The stereochemistry of both products is potential independent in contrast to their yield ratios. It is interesting to note the similar optical purity observed for RH derived from reduction of RBr in the presence of iodide ion (average of 7.4%, Table IV) and that derived from reduction of RI in bromide ion (average of 3.6%).

The reduction of RHgBr in acetonitrile–TEAB at a mercury cathode at −2.90 V gave an exponential *I-T* curve. The product from optically active RHgBr ($[\alpha]_{Hg} = -135°$) was optically pure RH ($[\alpha]_{Hg} = +147°$) plus a trace of R_2Hg. Reduction of racemic RHgBr under the same conditions, except that the potential was −1.30 V, yielded R_2Hg as the major product with a trace of RH. Succinonitrile was detectable in the reaction mixture by tlc and glc. By contrast, it was not found in the reduction mixtures produced from RBr, RI, or RHgBr in the high potential experiment. This may indicate that the reduction of cyanomethyl radical becomes rapid above −1.30 V *vs.* Ag-AgNO$_3$ in acetonitrile.

The controlled potential electrolysis of racemic 1-bromo-1-methoxymethyl-2,2-diphenylcyclopropane (**6**) produced 1-methoxymethyl-2,2-diphenylcyclopropane and the exocyclic olefin (**8**). The reduction consumed 1.88 F/mole of **6** and yielded a current–time curve similar to that observed with RBr.



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Discussion

Although the electrochemical reduction of organic halides has been studied extensively, there is at present no broadly accepted detailed mechanism for the reaction. We suggest that a generally applicable scheme for cathodic reduction of organic halides is more complex than has usually been assumed. The relative importance of prominent features of the reaction is greatly affected by variations in the nature of the reactant and electrode. We shall discuss the reaction of cyclopropyl bromide and of cyclopropyl iodide separately.

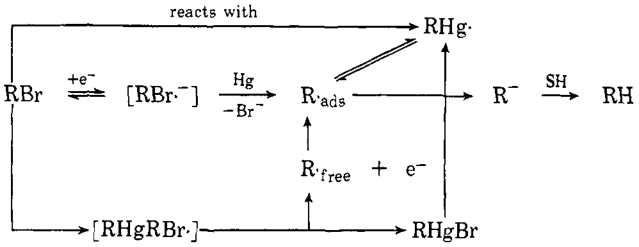
Reduction of 1-Bromo-1-methyl-2,2-diphenylcyclopropane. The stoichiometry of this reaction is well known to be that indicated in eq 4. Our results show,

$$\mathrm{RBr} \xrightarrow[+\mathrm{H}^+]{+2\mathrm{e}^-} \mathrm{RH} + \mathrm{Br}^- \qquad (4)$$

however, that at a mercury electrode, the reaction involves an organomercury intermediate which is reactive under the electrolysis conditions, being reduced to the hydrocarbon, RH. This suggestion is based upon kinetic observations during controlled potential reduction at macroelectrodes and upon chemical analyses of samples taken during reactions.

The proposed reaction scheme is shown in Chart I.

Chart I



It involves a series of reactions, including, a reversible one-electron formation of a short-lived ion radical $[\mathrm{RBr}\cdot^-]$ which decomposes to give a bromide ion and an adsorbed radical $[\mathrm{R}\cdot]_{\mathrm{ads}}$. This takes a second electron to form a carbanion $[\mathrm{R}^-]$ which is protonated to yield RH.

The adsorbed radical may also be in equilibrium with free alkyl mercury [RHg·] which can abstract a bromine atom from the substrate, forming RHgBr and a free alkyl radical. This radical is adsorbed on the electrode and the RHgBr is reduced to [RHg·]. Thus, once started, the removal of RBr is autocatalytic around the path involving [RHg·], RBr, and RHgBr.

The relationship between reaction current and reactant concentration during a constant potential electrolysis can be described empirically but reasonably accurately by the Nernst diffusion layer model.[19] For an electron transfer process that exhibits no kinetic complications, a first-order relationship between reactant concentration and current should exist.[20] With the equipment used in the present work, a reasonably linear relationship is observed. With more complex reactions, however, the current is proportional to the sum of the concentration of products times *n* for all system components that are reacting. We suggest that the observed current-time relationship is that which would result if a first-order electron transfer process

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(19) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, p 217.

(20) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1958, p 222.

and an autocatalytic process, itself involving an electron-transfer step, occurred simultaneously.

Taking this in the context of the details of the present reaction scheme, we are suggesting that in the sequence of steps RBr to $[\mathrm{RBr}\cdot^-]$ to $[\mathrm{R}\cdot]_{\mathrm{ads}}$ to $[\mathrm{R}^-]$ to RH, the first is rate determining. In the absence of the catalytic reaction, first-order kinetics would have been observed. In support of this, a linear log current–time decay was obtained for reduction of RBr at a glassy carbon electrode. At a mercury electrode the measured current is the sum of the two one-electron steps in reduction of RBr and the one-electron step in the reduction of catalytically generated RHgBr.

This reaction scheme could account for the difference observed in Figure 1 between the shape of the current–time curve 1 and the concentration–time curve 2 for RBr. The rate of production of RH (curve 3) is smaller during the first part of the experiment than is the rate of disappearance of RBr. The proposed scheme accounts for this. It is consistent with the observation of mercury compounds during, but not at the end, of the reaction and it would involve two electrons per molecule of RBr, as is observed.

In addition to hydrocarbon, the other products detected were triethylamine and ethylene. We suggest that they are formed during the process of protonating the carbanion in the final step of the proposed scheme. The carbanion, a strong base, could be protonated by the solvent or by the supporting electrolyte. To determine the identity of the proton source, reduction of RBr was carried out in TEAB–$\mathrm{CD_3CN}$ solution. The hydrocarbon produced showed 75% RD, indicating that much of the carbanion reacts directly with the solvent, presumably forming cyanomethylene anions. Both $[\mathrm{R}^-]$ and $[\mathrm{CH_2CN}^-]$ could be protonated by a tetraalkylammonium ion in a reaction like that indicated in eq 5.

$$\mathrm{R}^- + \mathrm{Et_4N}^+ \longrightarrow \mathrm{RH} + \mathrm{Et_3N} + \mathrm{CH_2{=}CH_2} \qquad (5)$$

Reduction of 1-Iodo-1-methyl-2,2-diphenylcyclopropane. The reaction of RI produces RH and the decomposition products from the supporting electrolyte. It also involves the same type of current–time relationship illustrated in curve 1 of Figure 1. It differs from the reduction of RBr, however, in that significant yields of the dialkyl mercury, $\mathrm{R_2Hg}$, are recovered and that the value of n is less than 2. Both the yield of $\mathrm{R_2Hg}$ and the value of n are potential dependent, as indicated in Tables V and VI. As the potential is increased, the value of n approaches 2 and the yield of $\mathrm{R_2Hg}$ decreases.

The same reaction scheme proposed for RBr reduction is appropriate if the reaction of $[\mathrm{RHg}\cdot]$ shown in eq 6 is included. The formation of $\mathrm{R_2Hg}$ and the

$$2\mathrm{RHg}\cdot \longrightarrow \mathrm{R_2Hg} + \mathrm{Hg}^0 \qquad (6)$$

potential dependence of its yield and of the n value can be understood if the implications of the low reduction potential for RI, compared with that for RBr are considered. At the low potential required to reduce RI, the rates of reduction of $[\mathrm{R}\cdot]_{\mathrm{ads}}$ and of RHgBr are much slower than they are at the potential required for RBr reduction. Consequently, the concentration of $[\mathrm{RHg}\cdot]$ can become large enough to make reaction 6 significant. As the reaction potential is increased, the rate of reduction of $[\mathrm{RHg}\cdot]$ is increased causing n to increase and the yield of $\mathrm{R_2Hg}$ to drop off. Even at the potential required to reduce RBr, there is some formation of $\mathrm{R_2Hg}$ from RI. This is caused by the fact that the reduction rate for RI is also potential dependent, so that the concentration of $[\mathrm{R}\cdot]_{\mathrm{ads}}$ produced at high potential from RI is much larger than that produced from RBr.

Cyclic Voltammetry. The cyclic voltammetry curves show an irreversible reduction peak (peak A) which corresponds to the wave obtained on dc polarography of the same compound. In addition, a product from this reaction can be oxidized and reduced at more positive potentials (peaks B and C). We suggest that while the electrode potential is in the region of peak A, the reaction described in Chart I is taking place. The products formed are unreactive and do not contribute to the currect. Both $[\mathrm{R}^-]$ and $[\mathrm{R}\cdot]_{\mathrm{ads}}$ would be reactive, however, the concentration of $[\mathrm{R}^-]$ is probably much larger than that of $[\mathrm{R}\cdot]_{\mathrm{ads}}$.

The B peak is therefore attributed to an anodic process involving the carbanion. The effect of proton donors in suppressing the B peak supports this suggestion. Similarly, the disappearance of the B–C peaks from RBr when RHgBr is added is understandable because rapid formation of unreactive $\mathrm{R_2Hg}$ would be expected from $[\mathrm{R}^-]$ and RHgBr.

At present, we cannot definitely identify the reaction responsible for the B peak. It involves the carbanion and it produces a species which is easily reduced to form the C peak. This process is not reversible: this is shown by the separation in potential between the B and C peaks (Table I) and by their shapes. One possibility is that peak B is caused by oxidation of $[\mathrm{R}^-]$ to the uncharged radical (eq 7). The fact that the

$$\mathrm{R}^- \longrightarrow \mathrm{R}\cdot + e^- \qquad (7)$$

B–C peaks in the RBr voltammogram are not caused by halves of a reversible couple shows that if reaction 7 is responsible for the B peak, the radical must undergo rapid conversion to some compound which is reducible at the potential of the C peak. If $[\mathrm{R}\cdot]$ persisted, reversible reduction to $[\mathrm{R}^-]$ would be expected.

It can be determined that this subsequent reaction is not a simple reaction of $[\mathrm{R}\cdot]$ with mercury to form $[\mathrm{RHg}\cdot]$. It has been shown that alkylmercuric halides undergo reduction in two steps, the first a reversible one-electron reduction to alkylmercury, shown in eq 8

$$\mathrm{RHgBr} \overset{+e^-}{\rightleftharpoons} \mathrm{RHg}\cdot + \mathrm{Br}^- \qquad (8)$$

$$\mathrm{RHg}\cdot \xrightarrow{+e^-} \mathrm{Hg}^0 + \mathrm{R}^- \xrightarrow{\mathrm{HS}} \mathrm{RH} \qquad (9)$$

and the second an irreversible one-electron reduction to the carbanion, shown in eq 9.[21,22] Our voltammetric results (Table I) and constant potential electrolysis results are in agreement with these previous reports. Accordingly, if peak B for RBr were reaction 7 followed by reaction with mercury, peak C would occur at −2.57 V, rather than at −1.58 V.

A second possible explanation is that peak B is caused by reaction 7, but that $[\mathrm{R}\cdot]$ undergoes an irreversible ring opening to produce a radical which is reduced to give peak C. This explanation encounters

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(21) N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 34 (1963).

(22) (a) R. Benesch and R. E. Benesch, *J. Chem. Soc.*, 960 (1923); (b) R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 460 (1966); (c) B. Gowenlock, *J. Chem. Soc.*, 535 (1958).

difficulty when one considers that all monosubstituted alkyl halides examined, including straight-chain compounds, show qualitatively similar behavior.

Another rationale for the B peak is that it is caused by a mercury dissolution reaction analogous to that responsible for anodic waves which are observed with halides at mercury electrodes. Such a reaction could lead to Hg(I) or to Hg(II) compounds. If Hg(I) is formed, the reaction would be that indicated in eq 10.

$$\mathrm{Hg} + \mathrm{R}^- \xrightarrow{-e^-} \mathrm{RHg}\cdot \qquad (10)$$

The objections to this are the same as those for direct oxidation of R$^-$ followed by combination with mercury. If Hg(II) were formed, the product would be R_2Hg, which is unreactive. Accordingly, we cannot be more specific about the B peak than to suggest that it involves the carbanion. About the C peak, we can only say that it appears to result from reduction of a product produced either in the A or B reactions.

Stereochemistry. As we have indicated earlier, the cyclopropyl system was chosen for investigation because it was anticipated that the stereochemical results would provide us with some insight into the mechanisms of electrochemical reduction of alkylhalides. Our results have shown that the reaction is not a simple one, and that the stereochemistry can be influenced by almost every parameter involved in the reaction, *i.e.*, solvent, electrolyte, electrode, leaving group (Br, I, HgX), extent of reaction, and substituents at the reaction site.

It can be seen from results shown in Table II that the reduction of (+)-(*S*)-RBr at a mercury electrode leads to the formation of (−)-(*R*)-RH in good yield, with overall retention of configuration and an optical purity of *ca.* 25%. However, when the reduction is carried out to 50% completion, then the optical purity of the product is only 13%. Reduction at carbon, in which nonexponential *I–T* curves and organomercury intermediates are not involved, led to 47% optically pure RH. This suggests that there is some mechanism of racemization prior to the formation of any organomercurial intermediates or carbanions.

It has recently been demonstrated[23] that the 1-methyl-2,2-diphenylcyclopropyl radical disproportionated within a solvent cage and that this resulted in the formation of RH which was *ca.* 37% optically pure. If it is assumed that reduction of a caged radical (RBr·$^-$) occurs more rapidly than disproportionation, then the optical purity of RH could rise to 47%. This assumption is reasonable since the electrode could be considered part of the cage and the activation energy for the reduction of the radical is undoubtedly smaller than for disproportionation. Interestingly enough, when the reduction of RBr is carried out under dissolving metal conditions,[24] in which the caged radical is also believed to be involved, and where one has a high concentration of solvated electrons, the optical purity of RH is 43–49%.[25]

When mercury is used as the electrode instead of carbon, it is suggested that the formation of [R·$_{ads}$] competes with the direct reduction of [RBr·$^-$] since mercury is a good radical trap.[26] The subsequent reduction or [R·$_{ads}$] to the carbanion [R$^-$] could lead to RH with an optical purity at least equal to, if not greater than, the 47% observed on carbon. However, this is not the case, since the experimentally observed value is 25%. This lowering of optical purity is due, we suggest, to the autocatalytic reaction. The [R·]$_{ads}$ is in equilibrium with [RHg·] (see Chart I) which reacts with RBr to form RHgBr and [R·]$_{(free)}$.[27] The [R·]$_{(free)}$ undergoes complete racemization before reduction to carbanion. This mechanism would be consistent with the lower optical purity of RH (25%) as well as the observed nonexponential *I–T* curve.

The autocatalysis by [RHg·] would also account for the low optical purity of RH (13.5%) when the reduction is interrupted near 50% completion. This is probably due to a change in the proportions of cyclopropyl moieties moving along the autocatalytic and direct reduction paths (see Chart I). In the latter stage of the reaction, the autocatalysis mechanism, being dependent on the concentration of RBr and [RHg·], becomes less important as the concentration of RBr drops, and the optical purity rises as a result.[28]

The reduction of (−)-(*R*)-RI generated the same type of *I–T* and cyclic voltammetry curves as RBr. However, there are major differences in the nature of the products and in the optical purity of RH as is shown in Tables V and VI. Bis(1-methyl-2,2-diphenylcyclopropyl)mercury (RHgR) is formed in addition to RH at controlled potentials from −2.10 to −2.90 V *vs.* Ag/Ag$^+$. The optical purity of RH was 3.9% at −2.16 V and 3.2% at −2.80 V, but RHgR was racemic in both cases.

The decrease in optical activity of RH in going from RBr to RI may be associated with the greater stability of the initially formed radical anions,[29] where [RI·$^-$] > [RBr·$^-$]. If [RI·$^-$], formed by a reductive attack on carbon from the halogen side of RI, is more stable, its longer lifetime would permit it to racemize by diffusion and formation of [R·]$_{free}$ (a rapidly inverting radical). The greater retention of configuration in RH from RBr, compared to that from RI, is in accord with the reaction of lithium[10b] and magnesium[10a] metals and solutions of sodium in liquid ammonia[24] with these alkylhalides.

The formation or RHgR from RI, when reduced at the same potential (−2.90 V *vs.* Ag-Ag$^+$) as RBr, is accounted for by the potential dependence of the initial electron transfer and the reduction of [R·]$_{ads}$.

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[23] H. M. Walborsky and C.-J. Chen, *J. Am. Chem. Soc.*, **89**, 5499 (1967).

[24] H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *ibid.*, **90**, 5222 (1968).

[25] An alternative explanation for the stereospecificity is the shielding by the electrode. An electrode-shielded radical, formed by reductive attack on carbon from the halogen side of RBr, is not racemized simply by becoming planar. Racemization occurs only when the planar radical undergoes a molecular rotation, a slow process relative to inversion. In other words, the mechanism of racemization prior to the formation of organomercurials is thought to be due to the rapid inversion (10^8–10^{10} sec^{-1}) and molecular rotation of (RBr·$^-$) before reduction to the carbanion.

[26] W. A. Waters, "Vistas in Free-Radical Chemistry," Pergamon Press, New York, N. Y., 1959, p 229.

[27] The abstraction of halogen from RBr by RHg· and other organometallic radicals is not without precedent;[20] see also O. A. Reutov, *Angew. Chem.*, **72**, 198 (1960). H. M. Walborsky and C.-J. Chen [unpublished results] reduced optically active RBr with triphenyltin radical and obtained racemic RH.

[28] Since the optical purity is only 13% at 50% completion, it will have to rise sharply to average out to 25%. If the autocatalysis pathway is slowly phased out, the optical purity of RH from direct reduction of RBr will have to approach the 47% value obtained on a carbon electrode.

[29] N. S. Hush and G. A. Segal, *Discussions Faraday Soc.*, **45**, 23 (1968).

Since RI can be reduced at a low potential (−2.10 V), this slows down the reduction of the adsorbed radical to carbanion R^- and allows the formation of $[RHg\cdot]$, which is subsequently converted to RHgR. The observation that RHgR is racemic is in agreement with the findings of Dessy, *et al.*,[22b] and Gowenlock[30] on the reduction of optically active *s*-butylmercuric bromide to racemic bis(di-*s*-butyl)mercury. The formation of optically pure RH, with retention of configuration, from RHgBr *via* reduction of $[RHg\cdot]$, indicates that either racemization of R in $[RHg\cdot]$ is slow, relative to reduction, or that racemization occurs by inversion[10a] ($RHg{-}{-}{-}R{-}{-}{-}Hg \rightarrow RHgR + Hg\cdot$).

An unusual effect of iodide ion was noted in Table IV. Reduction of RBr in DMF, containing iodide ion (TBAI), gave RH, with an optical purity very similar to that observed from RI, 7.9% and 3.5%, respectively. A conversion of RBr to RI under the reaction conditions is ruled out by the fact that RBr can be recovered from an incomplete reaction and by the known resistance of cyclopropyl halides to S_N2 displacement. The iodide ion must, therefore, exert its influence after the initial electron transfer by interacting with some intermediate such as $[RBr\cdot^-]$ to produce $[RI\cdot^-]$. It should be noted that this effect seems to be solvent dependent, since it is not observed in ethylenediamine. A change in solvent can also have an effect on the optical purity of RH in the reduction of RBr. It can be seen from Tables II and IV that the optical purity of RH, in the absence of the iodide ion effect, changes from *ca.* 25% in acetonitrile and DMF to 5% in ethylenediamine to completely racemic in dimethoxyethane.

The reduction of (−)-(*R*)-1-bromo-1-methoxymethyl-2,2-diphenylcyclopropane proceeded with net retention of configuration and gave (+)-(*S*)-1-methoxymethyl-2,2-diphenylcyclopropane, 31% optically pure in 89.5% yield along with 6.7% of the exocyclic olefin. The stereochemical results of this reduction are very similar to those observed for RBr. The slight (6%) increase in optical purity of the product, compared to RH, could be due to a faster rate of reduction of $[R\cdot]$ resulting from a lower reduction potential of $[R\cdot]$ caused by the electron-withdrawing methoxy group. The exocyclic olefin is formed by the elimination of methoxide from the carbanion.

All the reductions studied by us have resulted in overall retention of configuration. However, this need not always be the case, since by changing the substituent at the reductive center from a methyl group to a carbomethyoxyl or carboxyl group, the resulting product was optically active (30–40%), but the configurations were inverted.[9a,b] Grabowski[9d] has also found that the product from the reduction of optically active 2-phenyl-2-chloropropionic acid had an inverted configuration. Rationales for these observations have been given elsewhere.[9a,b]

Experimental Section

Cyclic Voltammetry. Cyclic voltammetry experiments were performed using apparatus previous described.[31] Sweep rates were 5–25 V/sec, with 3-m/sec step width. The electrodes employed were a mercury-plated platinum wire cathode, a reference electrode, and a platinum wire anode. The reference electrode was either a sce or a Ag/0.10 *M* $AgNO_3$-acetonitrile electrode. These reference electrodes were also used in the controlled-potential electrolysis experiments. The reference solution made contact with the electrolysis solution through an asbestos fiber sealed in a glass probe. The Ag/Ag^+ electrode was periodically referred to an aqueous sce in separate measurements. Voltammetric curves were recorded using unthermostated cells in a room having ambient temperature at 22°.

Constant-Potential Electrolyses. A fast-rise, three-electrode potentiostat (Wenking Model 61RH) was used for exhaustive controlled-potential electrolysis. All electrolysis cells were constructed to permit use of vacuum line techniques for handling solutions. Large-scale electrolyses were performed in H cells with either a mercury pool or glassy carbon cathode and a silver anode. Solutions were degassed by repeated freezing and pumping and were stored under a nitrogen or helium atmosphere.

Solutions were 0.10 *M* in TEAB, 2–5 m*M* in reactant for cyclic voltammetry, and 3–10 m*M* for exhaustive electrolyses.

Coulometry was carried out using a nitrogen–hydrogen coulometer as described by Lingane.[20] Current during exhaustive electrolysis was recorded on a strip chart recorder by monitoring ir drop across a suitably placed resistor in series with the electrolysis cell.

Product Analyses. Optical rotations were measured at the 5461-Å mercury line using a Bendix-Ericson Model 143A polarimeter equipped with a Texas Instrument Model FWS strip chart recorder. The instrument was equipped to read full chart on the following scales; 0–0.500 ± 0.001°, 0–0.100 ± 0.0002°, 0–0.050 ± 0.0002°, 0–0.010 ± 0.0003°, and 0–0.0005 ± 0.0003°. All nmr spectra were obtained using a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

An F & M Model 500 temperature programmed gas chromatograph with a thermal conductively detector was used for routine analysis of products. Most analyses were performed on a 2 ft × 0.25 in. copper column packed with 20% cyanoethylsucrose on 60/80 Chromosorb W at 100–125°. Analyses of dilute crude reaction mixtures were performed on an Aerograph Hi-Fi equipped with a hydrogen flame detector. All melting points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 137 or Model 237 infrared spectrophotometer. Brinkman silica gel $PF_{366+254}$ was used for analytical and preparative thin layer chromatography.

Reagents. The acetonitrile used in all electrochemical experiments was carefully purified according to a procedure previously described.[32] The dimethylformamide used was freshly opened spectrograde material. Dimethoxyethane was obtained from a center cut of a distillation over $LiAlH_4$. Ethylenediamine was stored over sodium until blue, then distilled and a center cut taken.

The tetraalkylammonium salts used as supporting electrolytes were purified by crystallization from a suitable solvent and carefully dried under vacuum.

Synthesis and Resolutions. (+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane (**1**) and (−)-1-iodo-1-methyl-2,2-diphenylcyclopropane (**2**) were prepared by a procedure previously described.[10a]

(+)-(*S*)-1-Methoxymethyl-2,2-diphenylcyclopropane. A solution of potassium *t*-butoxide was prepared under an argon blanket by allowing 0.500 g (12.8 × 10^{-3} mol) of potassium to react completely in 15 ml of *t*-butyl alcohol. (+)-(*S*)-2,2-Diphenylcyclopropylcarbinol, 0.60 g (2.65 × 10^{-3} mol), prepared from optically pure (+)-acid,[11,33] was dissolved in 5 ml of *t*-butyl alcohol and added to the solution of potassium *t*-butoxide. This mixture was allowed to stir for 15 min, then 3 ml of methyl iodide was added. The resulting mixture was stirred at room temperature for 20 hr, poured into water, and extracted with ether. The ether solution was dried over sodium sulfate and evaporated to yield 0.62 g (99%) of a colorless oil. This oil was applied to a 40 × 20 × 0.2 cm preparative thin layer chromatography plate and developed with 1:1 *n*-hexane–$CHCl_3$. The purified oil was collected from the plate and placed under vacuum for several hours. Analysis by gas chromatography of the neat oil failed to detect any solvent or impurities. The purified sample gave $[\alpha]^{27}_{5461}$ +181.5° (*c* 0.388, hexane); ir (film) 1600, 1500, 1450, 1410, 1200, 1110, 750, and 700 cm^{-1}; nmr (CCl_4) δ 1.00 and 1.21 (both broad singlets, 2, ring CH_2), 1.55–2.20 (complex, 1, ring *CH*), 2.70–3.40 (complex, 2, $-CH_2O$), and 6.90–7.60 ppm (complex, 10, Ar*H*).

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[30] For a discussion of the mechanism for racemization, see ref 21c.

[31] C. K. Mann, *Anal. Chem.*, 37, 326 (1965).

[32] J. F. O'Donnel, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

[33] H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Am. Chem. Soc.*, **83**, 2517 (1961).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.52; H, 7.58.

(−)-(*R*)-1-Bromo-1-methoxymethyl-2,2-diphenylcyclopropane. A solution of potassium *t*-butoxide was prepared under an argon blanket by allowing 1.14 g of potassium to react completely in 31 ml of *t*-butyl alcohol. (−)-(*R*)-1-Bromo-2,2-diphenylcyclopropanecarbinol (2.50 g), prepared from optically pure (−)-(*R*)-acid,[11,33] was dissolved in 10 ml of *t*-butyl alcohol and added to the solution of potassium *t*-butoxide. This mixture was allowed to stir for 15 min, then 7.0 ml of methyl iodide was added. The resulting mixture was stirred at room temperature for 20 hr, poured into water, and extracted with diethyl ether. The ether solution was dried over magnesium sulfate, and evaporated to yield a crystalline material. This material was recrystallized twice from methanol to yield 2.20 g (84%) of product: mp 103.5–104.5°; $[\alpha]^{26}{}_{5461}$ −97.5° (*c* 0.765, $CHCl_3$); ir (CCl_4) 1600, 1495, 1450, 1390, 1200, 1110, and 700 cm^{-1}; nmr (CCl_4) δ 1.80 (q, 2, J = 6 Hz, ring CH_2), 3.31 (q 2, J = 11 Hz, CH_2O), 3.2 (s, 3, CH_3O), and 7.05–7.65 ppm (complex, 10, Ar*H*).

Anal. Calcd for $C_{17}H_{17}OBr$: C, 64.36; H, 5.40. Found: C, 64.1; H, 5.5.

Halogen–Metal Exchange between 1-Bromo-1-methyl-2,2-diphenylcyclopropane (1) and *sec*-Butyllithium. The concentration of *sec*-butyllithium was determined by the double titration method of Gilman[34] and found to be 1.00 mequiv/ml. 1-Bromo-1-methyl-2,2-diphenylcyclopropane (**1**, 2.00 g, 6.97 mmol) was dissolved in 50 ml of dry diethyl ether contained in a vessel fitted with two serum caps. An argon atmosphere was maintained throughout the experiment. The ether solution of **1** was cooled in an ice–water bath. The *sec*-butyllithium was added in 1-ml increments. After each addition, the mixture was allowed to stir 45 sec before sampling. Samples of 0.2 ml were withdrawn with a 1-ml syringe and shot into dilute HCl. The hexane–ether layer was analyzed by gas chromatography. A total of ten samples was removed. A plot of the glpc data shows 8.0 mequiv of *sec*-butyllithium was required to exchange completely 6.97 mequiv of **1**.

(−)-1-Methyl-2,2-diphenylcyclopropylmercuric Bromide (4). Addition of 16 ml of a 1.00 *M* hexane solution of *sec*-butyllithium to 4.00 g (14 mmol) of optically pure ($[\alpha]^{27}{}_{5461}$ −130°) 1-bromo-1-methyl-2,2-diphenylcyclopropane (**1**) in 100 ml of dry ether over a period of 10 min at 0° under an argon atmosphere gave a yellow solution. This mixture was stirred for 15 min and then added to a slurry of 10.0 g (27.7 mmol) of mercuric bromide in ether at 0°. The addition required 30 min. The mixture was stirred for 4.5 hr and allowed to come to room temperature. The resulting reaction mixture was extracted with water, dried, and stripped to yield a solid residue which on crystallization twice from 75 ml of methanol gave 2.17 g (37%) of **4**: mp 205–206°; $[\alpha]^{26}{}_{5461}$ −135.37° (*c* 0.790, $CHCl_3$); ir (CCl_4) 1600, 1495, 1450, 1150, 1080, 706, and 695 cm^{-1}; nmr ($CDCl_3$) δ 1.38 (s, 3, CH_3), 1.70 (q, 2, J = 6 Hz, CH_2); 1.38 (d, J = 206.8 Hz, $CH_3C(Hg)<$), and 7.40 ppm (complex, 10, Ar*H*).

Anal. Calcd for $C_{16}H_{15}HgBr$: C, 39.59; H, 3.10. Found: C, 39.28; H, 3.34.

(±)-1-Methyl-2,2-diphenylcyclopropylmercuric Bromide (4) and (±)-Bis(1-methyl-2,2-diphenylcyclopropyl)mercury (5). Grignard reagent was prepared by refluxing 10.00 g (34.9 mmol) of (±)-**1** and 3.00 g (123.4 mmol) of magnesium metal in 80 ml of THF for 4.5 hr under an argon blanket. The Grignard solution was added to a slurry of 14.42 g (40 mmol) of mercuric bromide in 60 ml of dry THF. This resulted in a thick chalky white slurry which was allowed to stir at room temperature for 4 days. The reaction mixture was filtered and the filtrate evaporated to yield a slightly yellow viscous residue. Crystallization of this residue gave a solid, mp 152–165°, which yielded 6.81 g (40%) of **4**, mp 187.3–188.5° when recrystallized twice from high boiling petroleum ether.

The residue from the evaporation of the methanol mother liquor from above yielded 2.15 g (20%) of R_2Hg (**3**): mp 198–200°; ir (CCl_4) 1600, 1495, 1450, 1080, 845, 706, and 695 cm^{-1}; nmr (CCl_4) 1600, 1495, 1450, 1080, 845, 706, and 695 cm^{-1}; nmr (CCl_4) δ 1.00 (s, 3, CH_3), 1.29 (q, 2, J = 4.3 Hz, CH_2), 1.00 (d, J = 97.5 Hz, CH_3CHg), 7.20 ppm (complex, 10, Ar*H*). The ratio of methyl–mercury coupling constants for RHgBr (**4**) and R_2Hg (**5**) ($J_{RHgBr} = 2.12J_{R_2Hg}$) is in good agreement with the results of Wells and Kitching,[35] who found $J_{HgX} = 2.2J_{R_2Hg}$. This material gave a negative Beilstein test and yielded metallic mercury when heated at 273° for 15 min.

Anal. Calcd for $C_{32}H_{30}Hg$: C, 62.5; H, 4.9. Found: C, 63.0; H, 5.0.

Reductions. The apparatus and procedures used in the following reductions were discussed under Cyclic Voltammetry and Constant Potential Electrolyses.

Reduction of (+)-1-Bromo-1-methyl-2,2-diphenylcyclopropane (1) in Deuterioacetonitrile at a Mercury Electrode. A degassed 0.1 *M* solution of TEAB in CD_3CN was preelectrolyzed at −3.21 V *vs.* Ag/$AgNO_3$ until the current dropped to a constant 400 μA. A solution of 112.7 μmol of (+)-RBr (**1**) ($[\alpha]^{26}{}_{546}$ +130°) was injected into the cathode compartment and electrolyzed at −2.92 V *vs.* Ag/$AgNO_3$. The current was initially 50 mA, requiring 70 V across the cell, and dropped to a constant 300 μA after 80 min. Calculations from the coulometer readings gave an *n* value of 2.30 F/mole. The *n* value is higher than usual since the small quantity of CD_3CN could not be subjected to a rigorous purification procedure generally employed. The solution from the cathode compartment was reduced to 3 ml and applied to a 10 × 20 × 0.2 cm preparative tlc plate. The only band of material visible under uv (λ = 2540 or 3660 Å) was collected and eluted with methylene chloride to yield 0.019 g (92.5 μmol, 82%) of partially deuterated RH, $[\alpha]^{26}{}_{5461}$ −36.2° (*c* 0.26, $CHCL_3$). Based on the maximum $[\alpha]^{27}{}_{5461}$ (−150°) for nondeuterated RH, −36.2° is equivalent to 24.2% optical purity. The nmr spectrum of this material showed it to be 75% deuterated at the 1 position.[27] Mass spectra analysis indicated the same degree of deuteration. The infrared and nmr spectra of this material were identical with those of an authentic sample known to be 75.7% deuterated.

All other electrolytic reductions of RBr (**1**) listed in Table II, Table III, and Table IV were carried out in the same manner as described above. Any changes, such as addition of phenol, change of solvent, or electrolyte, or electrode, are indicated in the tables.

Reduction of (−)-1-Methyl-2,2-diphenylcyclopropylmercuric Bromide (4) at a Mercury Electrode. A degassed 0.1 *M* solution of TEAB in acetonitrile was preelectrolyzed at −2.90 V *vs.* Ag/Ag^+ until the current dropped to a constant 800 μA. A solution of 0.2269 g (463 μmol) of optically active RHgBr (**4**) ($[\alpha]^{26}{}_{5461}$ −135°) in a minimum amount of acetonitrile was injected into the cathode compartment and electrolyzed at −2.90 V. The current was initially 110 mA, requiring 82 V across the cell, and dropped exponentially to a constant 850 μA after 37 min. Calculations from the coulometer readings gave an *n* value of 1.2 F/mole. The cathode was removed, diluted with chloroform, and extracted with water. The $CHCl_3$ solution was stripped to yield an oil. Examination of this oil by tlc revealed two materials. The major component corresponded to RH and the minor component to a trace of R_2Hg (**5**).

The oil was distilled at 80° (0.25 mm) to yield 0.0335 g (35%) of RH, $[\alpha]^{27}{}_{5461}$ +150° (*c* 0.6702, $CHCl_3$) (optically pure). This material was shown to be pure and identical with authentic RH by glpc, tlc, and infrared spectroscopy. The above procedures were used in the reductions of (±)-RHgBr (**4**) at lower potentials.

Reduction of (−)-1-Bromo-1-methoxymethyl-2,2-diphenylcyclopropane at a Mercury Electrode. A degassed 0.1 *M* solution of TEAB in acetonitrile was preelectrolyzed at −3.00 V *vs.* Ag/$AgNO_3$ until the current dropped to a constant 600 μA. A solution of 146 μmol of **6** ($[\alpha]^{26}{}_{5461}$ −97.5°) in a minimum amount of acetonitrile was injected into the cathode compartment and electrolyzed at −2.90 V *vs.* Ag/$AgNO_3$. The current was initially 30 mA, requiring a 22.5 V across the cell, and dropped nonexponentially (similar to Figure 1) to a constant 200 μA after 90 min. Calculation from coulometer readings gave an *n* value of 1.88 F/mole. The catholyte solution was removed, diluted with water, and extracted twice with *n*-hexane. The hexane extracts were concentrated, applied to a 10 × 20 × 0.2 cm preparative tlc plate and developed with 1:1 $CHCl_3$–hexane. Two bands of material were visible under uv (λ 2540 Å). The faster band yielded 0.0311 g (89.5%) of 1-methoxymethyl-2,2-diphenylcyclopropane, $[\alpha]^{27}{}_{5461}$ +57.1° (*c* 0.62, hexane), optical purity 31.4%. The infrared and nmr spectra of this material were identical with those of an authentic sample.

The slower band from the tlc plate yielded 0.0020 g (6.7%) of 1,1-diphenyl-2,2-dimethylethylene. This material was shown to be identical with an authentic sample by glpc and infrared spectroscopy.

Reduction of (−)-1-Iodo-1-methyl-2,2-diphenylcyclopropane (2) at a Mercury Electrode. A degassed 0.1 *M* solution of TEAB in

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(34) H. Gilman and J. W. Morton, "Organic Reactions," Vol. VIII, John Wiley & Sons, New York, N. Y., 1954, Chapter 6.

(35) P. R. Wells and V. Kitching, *Tetrahedron Lett.*, 1029 (1964).

acetonitrile was preelectrolyzed at −2.16 V *vs.* Ag/Ag$^+$ until the current dropped to a constant 400 μA. A solution of 545.3 μmol of (−)-1-iodo-1-methyl-2,2-diphenylcyclopropane (**2**) ($[\alpha]^{26}{}_{5461}$ −199°) in a minimum amount of acetonitrile was injected into the cathode compartment and electrolyzed at −2.16 V *vs.* Ag/Ag$^+$. The current was initially 26 mA, requiring 19 V across the cell, and dropped nonexponentially (similar to Figure 1) to a constant 100 μA after 141 min. Calculations from coulometer readings gave an *n* value of 1.57 F/mole. The catholyte was concentrated and applied to a 40 × 20 × 0.2 cm preparative tlc plate and developed with $CHCl_3$–hexane 15:85. The two bands of material visible under 2540 Å uv were collected to yield 0.0740 g of R_2Hg (**3**) and 0.0635 g of RH. Analysis of (glpc) of the hydrocarbon fraction showed it contained 3.5 % of $Ph_2C{=}CMe_2$. The hydrocarbon fraction was applied to a 20 × 20 × 0.2 cm preparative tlc plate and developed with *n*-hexane. The RH band was collected to yield a colorless oil which was distilled in a micromolecular still yielding a pure sample of RH $[\alpha]^{26}{}_{5461}$ +5.9° (*c* 0.484, $CHCl_3$) (3.9% optically pure) with a glpc retention time and the infrared spectrum identical with those of an authentic sample. The R_2Hg (**3**) sample gave $[\alpha]^{26}{}_{5461}$ 0.0° (*c* 1.4800, $CHCl_3$), mp 198–200°. The infrared spectrum, nmr spectrum, and tlc R_f value were identical with those of an authentic sample: yields–1,1-diphenyl-2,2-dimethylethylene, 10.5 μmol, 1.9%; RH, 294.3 μmol, 54%; R_2Hg (**3**) 120.4 μmol, 44%.

The R_2Hg (**3**) sample (0.0740 g, 120.4 μmol) was dissolved in refluxing CCl_4 and bromine added until the color of the latter persisted. The reaction mixture was concentrated, applied to a 20 × 10 × 0.2 cm preparative tlc plate, and developed with *n*-hexane. The RBr (**1**) band was collected, eluted, concentrated and crystallized from methanol to give 0.033 g (48%) of RBr (**1**), mp 80–81°, and an infrared and nmr spectrum identical with those of an authentic sample.

A sample of 564.5 μmol of RI (**2**) ($[\alpha]^{26}{}_{5461}$ −199°) was electrolyzed at −2.80 V *vs.* Ag/Ag$^+$ and worked up by exactly the same procedure as given above to yield 0.0881 g (423.0 μmol, 75%) of RH $[\alpha]^{25}{}_{5461}$ +5.1°, 3.4% optically pure; 0.0027 g (12.9 μmol, 2.3%) of 1,1-diphenyl-2,2-dimethylethylene; 0.0291 g (47.3 μmol, 17%) of R_2Hg (**3**) $[\alpha]^{25}{}_{5461}$ 0.0°.

Mercury Analyses of RI (2) Reduction Products. Samples of RI (**2**) (103.9 μmol) were electrolyzed by the procedure described above at −2.10, −2.17, −2.37, −2.47, −2.50, and −2.90 V *vs.* Ag/Ag$^+$. The catholyte was concentrated and exhaustively oxidized with a mixture of concentrated sulfuric and nitric acid. The resulting solutions were treated with dithizone and the concentration of mercury was determined by colorimetric analysis.

Carbonium Ion Rearrangements in the Deltacyclane Ring System[1]

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Abstract: The acetolyses of *exo*- and *endo*-8-deltacyclyl brosylate, a mixture of *exo*- and *endo*-8-deltacyclyl chloride, as well as deamination of 8-deltacyclylamine in acetic acid, all lead to *exo*-8-deltacyclyl acetate (less than 0.4% *endo* epimer). Chlorodecarboxylation of deltacyclane-8-carboxylic acid with lead(IV) acetate and lithium chloride yields *exo*-8-deltacyclyl acetate (less than 0.4% *endo* epimer) and a mixture of *exo*- and *endo*-8-chlorodeltacyclane (the *exo*:*endo* ratio varies from 70:30 to 83:17). The rates of acetolysis of *exo*- and *endo*-8-deltacyclyl brosylate at 25.68° are 2.61 ± 0.09 × 10^{-4} and 4.62 ± 0.06 × 10^{-6} sec^{-1}, respectively. Acetolysis of *exo*-8-deuterio-*endo*-8-deltacyclyl brosylate yields *exo*-8-deltacyclyl acetate with deuterium scrambled between the *endo*-C-8 and C-4 positions, with deuteration predominating at the *endo*-C-8 position, while acetolysis of *endo*-8-deltacyclyl brosylate (69% deuteration at the C-9 positions) generates *exo*-8-acetate with 45% rearrangement of the deuterium to the C-5 positions. Acetolysis of *endo*-8-deuterio-*exo*-8-deltacyclyl brosylate results in *exo*-8-acetate in which the deuterium is scrambled between the *endo*-C-8 and C-4 positions, while acetolysis of *exo*-9-deuterio-*exo*-8-deltacyclyl brosylate produces *exo*-8-acetate in which 50% of the deuterium content has been scrambled into the C-5 position. The nmr spectra of fluorosulfonic acid–sulfur dioxide solutions of *exo*- and *endo*-8-deltacyclanol were measured and found to be identical, exhibiting absorptions at τ 4.83, 7.08, 7.50, 7.83, and 8.23 in the ratio of 2:2:2:1:4. An analysis of the acetolysis of optically active *endo*-8-brosylate reveals that *exo*-8-acetate is formed with 57% racemization, while acetolysis of optically active *exo*-8-brosylate produces *exo*-8-acetate with 99% retention of optical activity. The mechanistic implications of these results are discussed.

At the time this work was initiated, the deltacyclane (tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane)[3] ring system, which serves as the basic structural unit for the mixture of nitrile epimers (**1**-CN, **2**-CN) obtained in the homo-Diels–Alder condensation of acrylonitrile with norbornadiene, had not been extensively studied due to the low yields previously encountered in the synthesis of useful intermediates.[4] It was felt that if a good synthetic scheme could be developed for the syntheses of suitable *exo*- and *endo*-8-substituted deltacyclane substrates (**1** and **2**), an investigation of their solvolytic properties would be an especially interesting problem. The deltacyclane ring system incorporates both the nortricyclene (carbons 1, 2, 4, 3, 7, 6, and 5) and norbornane (carbons 1, 2, 3, 7, 8, 9, and 6) ring systems, and, due to this unique skeletal structure, a double norbornonium ion **4**, as well as the more traditional norbornonium ions **3**, are possible intermediates to be expected in ionization reactions of substrates **1** and **2**. Our study of the deltacyclane ring system was facilitated by the development of a method for achieving the syntheses of addition products, which conceptually are the result of Diels–

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(1) Previously published in part in preliminary form: P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967).

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(3) The name deltacyclane has been suggested for tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane and deltacyclene for the related olefin tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (**16**) by A. Nickon, private communication; A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967); and H. R. Kwasnik, Ph.D. Thesis, Johns Hopkins University, 1966.

(4) H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960).