Electroorganic Chemistry. VII.† The Role of Mercuric Salts in the Electroreduction of Benzylic Bromides

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Received September 12, 1989

Electrodeposition of a variety of benzylic mono- and 1,3-di-bromides and of benzylmercuric halides at stirred mercury pool cathode leads to products that support a mechanism for the electrodeposition of bromides that involves organomercury(I) intermediates and perhaps mercury(I) dimers. Products formed in the presence or absence of strongly adsorbed but electrochemically indifferent species suggest that monomolecular versus bimolecular reactions of the adsorbed organomercury(I) intermediates or dimers are strongly influenced by the presence of such species and that in some cases the reaction can be directed to one or another final product, providing a measure of control in synthetic applications.

INTRODUCTION

It was observed more than two decades ago that the reduction of benzylmercuric halides on a mercury cathode proceeds stepwise in two 1-electron processes, following pre-ionization of the substrate. The reduction steps are illustrated by equations (1) and (2):

\[
\begin{align*}
\text{Br}^+ & \rightarrow \text{R}^- + \text{Hg}[0] \rightleftharpoons \text{RHg}^+ \quad \text{E}^1 \quad \text{eq (1)} \\
\text{R}^- & \rightarrow \text{R}^\cdot \quad \text{Br}^- \quad \text{eq (2)}
\end{align*}
\]

Dialkylmercurials are obtained as products at more anodic working potentials (eq. 3) and hydrocarbons are formed at more cathodic working potentials (eq. 4).

\[
\begin{align*}
2\text{R}^- & \rightarrow \text{R-R} \quad \text{eq (3)} \\
\text{R}^\cdot + \text{SH} & \rightarrow \text{RH} + \text{S}^\cdot \quad \text{eq (4)}
\end{align*}
\]

We had earlier invoked a mechanism like this but involving mercury(I) intermediates to account for the formation of dialkylmercurials from 1,2-di-bromides (eq. 5). The precursor of hydrocarbon products in these and related reactions appears to be the carbanion formed from mercury(I) intermediates (eq. 5). Recently Vieira and Paters have published a careful
study of the electroreduction of tert-butyl chloride which demonstrated that one electron and two electron reductions could be effectively separated by carrying out electroreduction just beyond the first \( E^2 \) or the second \( E^3 \) main polarographic wave, respectively. Bard and Merz have reinvestigated the electroreduction of allyl halides in non-aqueous media\(^7\) and suggest that the reduction of allyl bromides on mercury involve organomercury intermediates which are reduced further at or above potentials corresponding to the second polarographic wave.

In addition to proposing organomercurial intermediates in our earlier studies, we proposed further\(^1,4\) that the mercury(I) dimer might be involved in the formation of dialkyl mercurials and/or carbon-carbon dimers which are often found in the electroreduction of halides. According to a mechanism proposed by Jensen and Rickborn\(^8\) the organomercury(I) radical can undergo dimerization followed by a Wagner-Meerwein rearrangement and disproportionation to yield organomercury(II) species and mercury(0) (eq. 6). Evidence to support this view has been gathering for many years. Dessy has proposed the intermediacy of mercury(I) species\(^9\) and mercury(I) radicals adsorbed

\[
\text{RHg}^+ \rightarrow (\text{RHg})_2 \rightarrow \text{R}_2\text{Hg} + \text{Hg(0)}
\]

on metal surfaces have been commonly invoked.\(^{9b}\) Heaton and Laitinen have proposed a similar mechanism for the electroreduction of methyl mercuric halide.\(^{9c}\) Laviron and Roullier\(^{9c}\) have studied adsorbed radicals formed by the reduction of arylmercuric salts on mercury. Adsorbed intermediates such as those in equation 5 have been confirmed by Brown and Taylor\(^{9e}\) Symmetrization of such intermediates have been proposed by Reutov.\(^{9f,g}\)

**RESULTS AND DISCUSSION**

Voltammetric examination of 3-bromo-1-phenyl-1-propylmercuric bromide (1), formed in an electrocatalytic reaction\(^{10}\) from the reduction of 1,3-dibromo-1-phenylpropane (2) at low potential, showed two
reduction waves, $E_{1/2} = -0.33 \text{ V}$ and $E_{2/1} = -0.70 \text{ V}$ (versus see). Both of these waves are too anodic to be ascribed to the reduction of the terminal C-Br bond.\textsuperscript{11} On the other hand the voltammograms of a variety of benzylic bromides all exhibit three reduction waves. These compounds include 1-bromo-1-phenylethane (3), benzyl bromide (4), 1,3-dibromopropane (5), 1,3-dibromo-1,3-diphenylpropane (6), and 1,8-bis(bromomethyl)naphthalene (7). We believe that the first ($E_{1/2}^{1/3}$) (eq. 1) and third ($E_{2/1}^{3/2}$) (eq. 5b) waves originate from the same reduction steps as found in 1. Thus these wave would be due to the reduction of RHgBr (eq. 1) and RHg\textsuperscript+ (eq. 5b), respectively. The intermediate wave ($E^0$), at a potential slightly more anodic than that of $E^0$, but almost superimposed on it, is tentatively assigned to the reduction of the C-Br bond (eq. 5a). Similar voltammetric curves have been obtained by other workers for the reduction of benzylic halides,\textsuperscript{12,13} but their origin has not been rationalized. The products of exhaustive electroreduction of 1 at a stirred mercury cathode are shown in Table I. Consider first the reactions at $-2.10 \text{ V}$. The products, particularly 8 and 9, suggest existence of a long-lived carbanion which can be intercepted in a solvet of low $pK_a$\textsuperscript{15,16} An almost identical product distribution was obtained for the reduction of 2 at this very cathodic potential, suggesting a common intermediate.

Products from the reduction of 1 at $-1.70 \text{ V}$ require a more detailed discussion. Electroreduction of mono- and dihalides seldom leads to carbon dimers, but often leads to organomercury (II) dimers, especially at more anodic potentials.\textsuperscript{14,15} Those cases in which a significant amount of carbon dimer is found are cases for which the organic radical is exceptionally stable, or for which the organomercurial is not. This rationale satisfactorily explains the formation of exclusively 4,4'-dinitrobenzyl from the reduction of p-nitrobenzylbromide.\textsuperscript{16,17} Grimshaw\textsuperscript{17} reported also that the electroreduction of 3,4-dichlorobenzylbromide and m-bromobenzylbromide yielded dimers as the major products. Brown\textsuperscript{18a} and Bazier\textsuperscript{18} found, at certain potentials, small amounts of bibenzyl in the reduction products of benzyl bromide. Reduction of 1-bromoadamantane gives a small but reproducible amount of biadamantyl.\textsuperscript{19} The structure rules out an $S_N2$ reaction between carbanion and unreacted bromide as a likely source of dimer. Benzyl bromide itself provides an interesting case. It has been widely studied before.\textsuperscript{16,17}
### TABLE I

**Products of the Electroreduction of 3-Bromo-1-phenyl-1-propylmercuric bromide (I)**

<table>
<thead>
<tr>
<th>Potential V vs sce</th>
<th>Solvent</th>
<th>Trapping agent</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.10</td>
<td>DMFb</td>
<td>—</td>
<td>100</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>-2.10</td>
<td>80%/cAcOHc,d</td>
<td>—</td>
<td>17</td>
<td>83</td>
<td>—</td>
</tr>
<tr>
<td>-1.70</td>
<td>DMF</td>
<td>—</td>
<td>—</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>-1.70</td>
<td>DMF</td>
<td>Ph₃CHe</td>
<td>70</td>
<td>—</td>
<td>30</td>
</tr>
</tbody>
</table>

a Relative percent. All total yields were in excess of 90%.  
b 0.2 M Et₄NBF₄ as supporting electrolyte.  
c 10% of solvolitic products (benzyl alcohol and acetate) is included here.  
d 0.2 M AcONa as supporting electrolyte.  
e The ratio of Ph₃CH to substrate was 1.2/1.

Dibenzylmercury transforms slowly on standing at room temperature to dibenzyll, a previously reported primary reaction product, and mercury. The change is accelerated by light. Figure 1 shows the relative amounts of the two principles products obtained from the reduction as a function of the potential at which the reduction was carried out. When benzyl bromide itself is reduced, there is a smooth and expected transition from mostly dibenzylmercury at —0.8 V to toluene at —1.6 V. However, starting with benzylmercuric bromide, the main product is dibenzylmercury over the entire potential range from —0.8 to —1.6 V. If an S₈ mechanism were important here, a high yield of dibenzylmercury would be expected from benzyl bromide at moderately cathodic potentials, since both benzyl bromide and benzyl anion concentrations should be greatest then. Little dibenzylmercury would be expected from the salt. The reverse is seen to be true.

![Graph A](image)

![Graph B](image)

Figure 1. Percent Yields of Dibenzylmercury (○) and Toluene (□) from the Electroreduction of Benzyl Bromide (A) or Benzylmercuric Bromide (B)  
(0.033M substrate, 0.2M LiClO₄ in Acetonitrile).

Since benzylmercuric bromide is reduced much more easily than benzyl bromide in the first one-electron transfer at all potentials, the concentration of the intermediate [C₆H₅CH₂Hg·] is much greater starting with benzylmercuric bromide than with benzyl bromide, and the dimer derived from coupling prevails (eq. 1 and 6). Starting with 4 itself, the first electron transfer (eq. 5a) is much faster than the second electron transfer (eq. 5b), $k₁/k₂ > 1$.
at anodic potentials, leading to a large amount of coupling product. But the relative rates of the two processes become comparable at more cathodic potentials, so that more two electron product is obtained.

The process is further complicated by the ongoing electrocatalyzed production of benzylmercuric bromide at low potentials. Figure 2 illustrates this behavior. When unreacted starting material 4 is measured and plotted against current consumption for low and high negative potential reduction of benzyl bromide, the starting material disappears more rapidly relative to current consumption at $-0.8\,\text{V}$ than at $-1.4\,\text{V}$. The straight lines on the graphs represent the theoretically calculated current requirement to obtain the observed final product ratio at that potential (cf. Figure 1A). Production of the salt, benzylmercuric bromide, is not an electron consuming process. The difference between current consumed and benzyl bromide remaining is due to a non-volatile intermediate which is formed electrocatalytically. That intermediate is most likely benzylmercuric bromide. These findings are not without precedence. Rogers and Diefenderfer\textsuperscript{18b} reported the chemical decomposition of dibenzylmercury, the disappearance of benzyl bromide and the presence of benzylmercuric bromide, further concluding that a prior (chemical) reaction pre-
ceded the electron transfer step. Electrocatalytic generation of benzylmercuric bromide was earlier observed by Brown, Thirsk, and Thornton.\textsuperscript{18a}

Electroreduction of 1-bromo-1-phenylethane (3) gave 1-phenylethane as the exclusive product at $-1.60$ V. A voltmogram of 3 showed three waves: $E^1$ ($-0.86$ V), $E^2$ ($-1.32$ V), and $E^3$ ($-1.36$ V). These three waves must all be attributed to some structural features of the single C-Br bond. At a lower working potential ($-1.20$ V), (chosen to be below $E^2$ and $E^3$) reduction of 3 yields 2,3-diphenylbutane (90\%) and as a minor product, 1-phenylethane (5\%).\textsuperscript{21}

However, the carbon dimer is clearly not a primary reaction product. The thermal stability of 1-phenylethymercury derivatives at room temperature is low, and decomposition of these compounds to mercury(0) and carbon dimer has been observed during workup at $0^\circ$ C of a low temperature reaction\textsuperscript{24}. It seems likely therefore that the organomercury(II) dimer, formed according to equation 6, is the immediate precursor of carbon dimer (eg., Table I, compound 10) in other cases as well. Evidence for the presence of an organomercurial dimer (11) in the reaction mixture is clear (see Experimental Section) at higher potentials starting with 1. At lower potential 11 can be isolated as a major product from the electroreduction of 2.

**Table II**

Products from the Electroreduction of 1,3-dibromo-1-phenylpropane (2) at $-0.85$ V.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Supporting electrolyte\textsuperscript{a}</th>
<th>Trapping agent</th>
<th>Yield,%</th>
<th>n</th>
<th>Products,%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>DMF</td>
<td>Et$_4$NBF$_4$</td>
<td>—</td>
<td>68</td>
<td>1.01</td>
<td>24</td>
</tr>
<tr>
<td>DMF</td>
<td>Et$_4$NBF$_4$</td>
<td>PhCH$_2$OMe\textsuperscript{c}</td>
<td>62</td>
<td>1.19</td>
<td>40</td>
</tr>
<tr>
<td>DMF</td>
<td>Et$_4$NBF$_4$</td>
<td>—</td>
<td>61</td>
<td>1.28</td>
<td>51</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 0.2 M concentration.
\textsuperscript{b} Based on equivalents of substrate.
\textsuperscript{c} Substrate to trapping agent ratio was 1/1.2.

Products of the electroreduction of 1,3-dibromo-1-phenylpropane (2) have been reported\textsuperscript{1} and at $-1.2$ V and $-1.3$ V appear to be typically intramolecular $S_N$2 products. Neither benzylmethyl ether nor triphenylethane intercepted an intermediate when added to the reduction mixture of 1,3-dibromo-1-phenylpropane under these conditions. The reduction of this same dibromide (2) at $-0.85$ V leads to a different array of products (Table II), which includes two mercury containing species that arise from a one-electron reduction. At this potential also benzylmethyl ether fails to alter the array of products significantly. Indeed, the most noteworthy variation is a shift from ,,bimolecular“ (11) to ,,monomolecular“ (8) product, a change induced either by the addition of benzylmethyl ether or by the substitution of lithium perchlorate as supporting electrolyte. Interpretation of these results will be presented later. The absence of evidence for hydrogen atom transfer predicates against the presence of carbon free radicals during the reduction of benzylic bromides on a mercury cathode.\textsuperscript{22} It is more likely that mercury(I) intermediates are responsible for the potential dependent formation of carbon dimers from benzylic bromides at a mercury cathode. Baizer\textsuperscript{19} has
suggested that the bimolecular attack of R$^-$ on RHgBr can lead to the formation of carbon dimer. This idea cannot be ruled out except for the case of 1-bromoadamantane.$^{20}$ The unusual behavior of 1,3-dibromo-1-phenylpropane (2) in the presence of triphenylmethane (Table I) will be discussed later.

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{Br} \\
\text{Hg} & \\
\text{C}_6\text{H}_5 & \quad \text{Br}
\end{align*}
\]

![Image of molecular structure]

**TABLE III**

*Electroreduction of 1,3-Dibromo-1,3-diphenylpropane$^a$ (6) at -0.85 V.*

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Supporting electrolyte$^b$</th>
<th>Conc (M)</th>
<th>Trapping agent</th>
<th>Yield,% n</th>
<th>Products$^{c,d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>Et$_4$NBF$_4$</td>
<td>0.092</td>
<td></td>
<td>91</td>
<td>22.5</td>
</tr>
<tr>
<td>DMF</td>
<td>Et$_4$NBF$_4$</td>
<td>0.084</td>
<td>PhCH$_2$OMe$^e$</td>
<td>94</td>
<td>30.5</td>
</tr>
<tr>
<td>DMF</td>
<td>Et$_4$NBF$_4$</td>
<td>0.073</td>
<td>(PH)$_3$CH$^f$</td>
<td>61</td>
<td>20.0</td>
</tr>
<tr>
<td>AcOH$^e$</td>
<td>AcONa</td>
<td>0.093</td>
<td></td>
<td>90</td>
<td>45.2</td>
</tr>
</tbody>
</table>

$^a$ d,l/meso ratio 59:41.

$^b$ 0.2 M concentration.

$^c$ Relative percent.

$^d$ One to three percent by weight of an unidentified organomercurial was found in these cases.

$^e$ Substrate to trapping agent ratio was 1:1.3.

$^f$ Substrate to trapping agent ratio was 1:1.2.

$^g$ 80%/ Aqueous solution.

$^h$ Not meaningfull, solvent was extensively reduced.

Nearly exponential decay of current with time in the preparative reduction of I, indicates an apparent first order electrochemical process. Since overall two electrons are transferred, this implies that the ratio between the rate constants for the two 1-electron processes ($k_1/k_3$ in eq. 5) is much greater than 1. Identical chronoamperometric curves have been obtained for the electroreduction of 1,2-dibromides$^{23}$ and in the electroreduction of numerous monophenyl- and dibromides at very cathodic potentials.$^4$ Electroreduction of 1-phenyl-1-bromoethane (4) exhibits a different chronamperometric curve as reported earlier.$^{21}$ At low potential the current decreases to nearly zero and then rises again with time to a maximum later in the reaction. This behavior, and the nature of the products, are indicative of the electrocatalytic formation of organomercuric halide. Such behavior has been reported before.$^{24}$ These observations lead us to conclude that the source of RHg$^+$ and the subsequent carbanion formed during the electroreduction of benzyllic
halides at potential below $E^3$ is not only the original substrate but also organomercuric bromide formed electrocatalytically from the substrate. A central role for organomercurial salts in the electroreduction of halides is hence possible.

A different nonexponential current-time curve is found for the reduction of 4 at potentials between $E^1$ and $E^3$ and arises from the superposition of two processes that appear to be consecutive first order reactions. We suggest that the nonexponential chronocamperometric curves observed in the reduction of 4 at $-1.60 \text{ V}$ can be attributed to two consecutive one electron processes (eq. 5) if $k_3 > k_i$.

It will be noted that the presence of triphenylmethane in the the catholyte of the reduction of 1 strongly suppresses "bimolecular" reaction leading to dimerization (see Table I). This may be due to competitive adsorption of triphenylmethane on the polarized electrode surface, leading to a decrease in the concentration of adsorbed organomercurial salt and the mercury(I) intermediate which it produces. Unable to dimerize at the one electron reduction stage, the mercury(I) intermediate can be further reduced and undergo intramolecular cyclization to yield the observed cyclopropane (8). At low potential the direct reduction of benzyllic bromides does not lead to dimer as a primary product, but the dimer is produced through an organomercuric bromide which is itself formed electrocatalytically from the starting material. The introduction of indifferent strongly adsorbed species in a preparative electroreduction holds promise as a method of directing product in competing monomolecular or bimolecular products. This selective adsorption phenomenon is again apparent in the reduction of 2 (Table II), in which a small but clear shift toward "monomolecular" product (8) is observed when benzylmethyl ether is added, or when lithium perchlorate is substituted as a supporting electrolyte.

When 1,3-dibromo-1,3-diphenylpropane (6) is the substrate, the addition of benzylmethyl ether or triphenylmethane has no significant effect on the reaction. Even at $-0.85 \text{ V}$ no 1,3-diphenylpropane (13) was found, and a mixture of stereoisomeric 1,2-diphenylcyclopropanes (12c, 12t) was the almost exclusive product (Table III). This result is not unexpected if the starting dibromide 6 and subsequent intermediates remain strongly adsorbed on the electrode surface. Indeed, the addition of eaqueous acetic acid failed to intercept a canbanin and alter the yield of cyclopropane products. This behavior could be an example of mercury radical adsorbed on the mercury surface (eq. 7).
If d,l-6 leads to trans cyclopropane (12t) and meso-6 leads to cis cyclopropane (12c), then the product distribution suggests that once 6 is on the electrode surface it remains so until ring closure is complete. When the reduction of 6 is carried out at much higher potentials (Table IV) the cyclopropanes formed (12c, 12t) seem to suggest that the reaction has become somewhat less stereospecific, and may be undergoing a change in mechanism. At —2.15 V and low substrate concentration a substantial amount of 1,3-diphenylpropane (13) is formed, and it appears to form at the expense of the cis-cyclopropane product (12c).

**TABLE IV**

<table>
<thead>
<tr>
<th>Solvent&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Potential (V)</th>
<th>Conc. (M)</th>
<th>Trapping agent</th>
<th>Yield,&lt;sup&gt;%&lt;/sup&gt; n</th>
<th>Products,&lt;sup&gt;%&lt;/sup&gt;</th>
<th>12c</th>
<th>12t</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>—1.30</td>
<td>0.057</td>
<td>none</td>
<td>81</td>
<td>2.01</td>
<td>50.0</td>
<td>50.0</td>
<td>—</td>
</tr>
<tr>
<td>DMF</td>
<td>—2.15</td>
<td>0.025</td>
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<td>1.96</td>
<td>48.7</td>
<td>51.3</td>
<td>8.6</td>
</tr>
<tr>
<td>DMF</td>
<td>—2.15</td>
<td>0.020</td>
<td>none</td>
<td>71</td>
<td>2.00</td>
<td>39.2</td>
<td>50.8</td>
<td>10.0</td>
</tr>
<tr>
<td>DMF</td>
<td>—2.15</td>
<td>0.008</td>
<td>none</td>
<td>80</td>
<td>2.31</td>
<td>40.0</td>
<td>45.0</td>
<td>14.0</td>
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<sup>a</sup> d,l:meso ratio 59:41.
<sup>b</sup> 0.2 M concentration of Et<sub>4</sub>NBF<sub>4</sub>.
<sup>c</sup> Relative percent.

**TABLE V**

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Trapping agent&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield,&lt;sup&gt;%&lt;/sup&gt; n</th>
<th>Products,&lt;sup&gt;%&lt;/sup&gt;</th>
<th>14</th>
<th>15</th>
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<tr>
<td>—2.15</td>
<td>none</td>
<td>34</td>
<td>1.32</td>
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<td>63</td>
</tr>
<tr>
<td>—2.15</td>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;CHO&lt;sub&gt;Me&lt;/sub&gt;</td>
<td>71</td>
<td>1.84</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>—2.15</td>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;CH</td>
<td>59</td>
<td>1.77</td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td>—2.15</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>62</td>
<td>1.80</td>
<td>70</td>
<td>30</td>
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<tr>
<td>—2.50</td>
<td>none</td>
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<td>1.65</td>
<td>72</td>
<td>28</td>
</tr>
<tr>
<td>—2.50</td>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;CHO&lt;sub&gt;Me&lt;/sub&gt;</td>
<td>78</td>
<td>1.84</td>
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<tr>
<td>—2.50</td>
<td>anthracene&lt;sup&gt;c&lt;/sup&gt;</td>
<td>62</td>
<td>—</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

<sup>a</sup> All reaction were in DMF using 0.2 M Et<sub>4</sub>NBF<sub>4</sub> as supporting electrolyte.
<sup>b</sup> Substrate: trapping agent ratio 1:1.2.
<sup>c</sup> Relative percent. Yields were between 75 and 90%.

The role of adsorption, both of indifferent species and of the substrate, is an important one in product determination. Further evidence of this can be seen in the example below. Alkyl monohalides undorned by structural features which might enhance adsorption, have been reported to give little or no organomercurials. Whereas 1-bromo-3-phenylpropane when reduced at —2.50 V gives a mixture of 1-phenylbutane, 14 (28%) and di-1-(3-phenylpropyl)mercury, 15 (72%) (Table V), 1-bromobutane gives much less bimolecular coupling (eq. 8).
For reduction of 9, as seen in other cases, addition of indifferent strongly adsorbed species supresses bimolecular coupling, at both $-2.50$ V and $-2.15$ V. Taken alone these results could also be accounted for by postulating that benzylmethyl ether and triphenylmethane act solely as radical scavengers. Taken together with earlier published 1,ω-dibromide results\(^4\) and the dramatic shift toward intramolecular versus intermolecular reaction seen here for 1,3-dibromides, a selective adsorption process is suggested.

The most appropriate mechanism for the electroreduction of benzyl bromides is similar to that which has been proposed before:\(^1\,\text{ESI}\)

**SCHEME 1**

A bar over the formula denotes adsorption on the cathode surface.

Two separate pathways with different potential dependence can lead to adsorbed organomercury(I) radicals; direct reduction of the substrate, or reduction *via* the organomercuric salt formed in an electrocatalytic process.

It is possible to make some general statements on the reductive pathways for organic halides. Persuasive evidence has been presented suggesting that not all low potential reduction products arise from intermediate mercury(I) species. Peters\(^6\) has shown that 2-bromo-2-methylpropane yields a mixture of 2-methylpropane and 2-methylpropene when reduction is carried out at the first wave, and that the process appears to be a radical-radical disproportionation reaction. An earlier study of Peters and coworkers using...
1-bromodecane\(^{28}\) shows that decane can arise in a one-electron process involving hydrogen atom transfer from solvent. Wiberg and Epling have intercepted carbon radical species using a good radical scavenger.\(^{22}\)

An equilibrium is established after the first electron reduction (eq. 9) which is quite sensitive to the structure of the substrate and that both

\[
\text{RHg} \rightleftharpoons \text{R} + \text{Hg(0)} \quad \text{eq (9)}
\]
carbon and mercury(I) radicals are immediates, with the position of the equilibrium depending on the detailed structure of the species involved.

The ultimate disposition of the one-electron reduction species is complex and sensitive to a variety of factors. At strongly cathodic potentials the one-electron species are further reduced and products are typically those derived from carbonanions. At lower potentials substrates that yield relatively stable carbonanions and are not strongly adsorbed undergo disproportionation. Primary bromides yield little or no disproportionation, but at low potentials undergo hydrogen atom abstraction from solvent or from other good hydrogen atom donors. More strongly adsorbed species (eg., 1,ω-dihalides and aralkyl halides) give more mercury(I) coupling products under similar conditions. The cases involved in this study — benzylic halides — cannot yield disproportionation products and hence give mercury(I) coupling and carbonanion derived products almost exclusively. When monomolecular and bimolecular pathways can compete, addition of strongly adsorbed electrowactive species can alter the product distribution significantly.

**EXPERIMENTAL**

**General.** — Melting points and boiling points are uncorrected. \(^1\)H NMR spectra are recorded on a Varian EM 390 spectrometer using carbon tetrachloride, benzene-d\(_6\) or CDCl\(_3\) with internal TMS. \(^{13}\)C NMR data were obtained using a Brucker HX-90E spectrometer with DCD\(_3\) solution using a MS standard. Volatile liquids were analyzed by GLPC on a 4 meter Carbowax 20M column on Chromosorb W, 15\%/\(v\), with a Varian 90P chromatograph. Mass spectral data were collected from a Varian MAT CH-5 mass spectrometer. Thin layer chromatography was performed on 5 × 20 cm silica gel plates (1B-F flexible sheets) and were visualized by ultraviolet light.

Mercury was Bethlehem grade, recycled as previously described.\(^{23}\) Solvents were dimethylformamide (DMF) and acetonitrile and were purified prior to use and stored in the dark under dry nitrogen and over 5Å molecular sieve. DMF was purified as described previously.\(^{23}\) Acetonitrile (Fisher 99 mole \%(a) was purified by the following procedure. The solvent was stirred for 48 hours over calcium hydride and then distilled slowly under nitrogen. It was stirred over phosphorous pentoxide for two hours then redistilled. Tetraethylammonium fluoroborate (Southwest Analytical Chemicals) and lithium perchlorate were stored over phosphorous pentoxide and used without further purification. Other chemicals were reagent grade.

**Benzyl bromide** (4) (Matheson, Coleman and Bell) was distilled prior to use (bp 106 °C, 11 torr) and stored in the dark for short periods of time. NMR and GLPC showed that it was free of detectable impurities.

1,3-Dibromo-1-phenylpropane (2) was synthesized following an earlier procedure.\(^1\) It could be stored in a dessicant at 0 °C for several months. NMR and MS showed that its purity was greater than 98\%/\(v\).

3-Bromo-1-phenylpropane (9) (Aldrich Chemical Co.) was distilled (bp 108 °C, 11 torr). NMR and MS showed that purity was greater than 99\%/\(v\). It could be stored at 0 °C for at least six months.
1,8-Dibromo-1,3-diphenylpropane (6) was prepared by a procedure from our laboratory. NMR and MS showed that its purity was greater than 97%. It could be stored in a desiccator at 0°C for several weeks.

Dibenzylmercury was prepared by the exhaustive electroreduction of benzyl bromide at a mercury cathode in a divided cell. Acetonitrile (150 mL) with 0.2 M LiClO₄ was placed in the cell and 3.4 g (0.02 mol) of benzyl bromide was placed in the cathode compartment. Reduction was carried out at −0.7 V (vs SCE) until the current reduced to ca. 5% of its original value. The catholyte was removed, evaporated in vacuo to 1/5 of its original volume, cooled to 0°C, and poured onto ice. The solid which formed was removed by filtration, dried, and recrystallized from ethanol to give needles, mp 109.5–110.5°C (lit. 111°C).  

Instrumentation and Procedures. Analytical electrochemical measurements were carried out using a PAR Model 174A Polarographic Analyzer with drop controller and a Houston Instruments Omnigraphic 2000 XY Recorder. Preparative experiments were carried out with a PAR Model 373 Potentiostat/Galvanostat connected to a PAR Model 379 Digital Coulometer with IR compensation and a Simpson Multicorder 605 to provide a permanent record of the current versus time. A preparative electrochemical cell similar to one described previously was used in these electroreductions. In each case the solvent-supporting electrolyte system was prerelaxed at a potential 0.1V more cathodic than that of the planned run in order to reduce any remaining impurities. Prerelaxation was continued until the current fell to a steady value of several milliamperes. A constant slow stream of nitrogen was passed through the cell during electrolysis.

Product Analysis in the Electroreduction of 4. The electroreduction was carried out in the usual manner. During the reaction a dry nitrogen stream carried volatile products into a trap cooled by liquid nitrogen. The catholyte was cooled to 0°C and the contents of the liquid nitrogen trap were mixed with it after being brought to room temperature. In a cold room (+6°C) cold water was added (200 mL) and the aqueous mixture was extracted with freshly distilled Freon 11 (fluorotrichloromethane, bp. 23°C, Matheson Gas Products). Five portions of ca. 15 mL were used. After washing the combined extracts with water and drying over anhydrous magnesium sulfate, the solvent was evaporated using a Vigreux column at an ambient temperature of +6°C. The residue of distillation was examined by ¹H NMR in C₆D₆ solvent. To the sample in the NMR tube was added a carefully weighed amount of tert-butylbenzene as an internal standard. Yields were calculated from the spectrum on the basis of integral ratios of the standard versus reduction products. tert-Butylbenzene: NMR (CCL₄) δ 1.25 (s, 9H), 7.2 (m, 5H).

Product Analysis in the Electroreduction of Dibenzylmercury. The reduction of dibenzylmercury was carried out in the same manner as was benzyl bromide and similarly extracted with Freon 11. The Freon 11 removed by distillation through a Vigreux column at 30°C was examined by GLPC to assure the absence of other volatile materials. Residue remaining in the flask after the removal of Freon 11 was distilled at room temperature in vacuum (< 0.1 Torr), the volatile part being collected in an efficient liquid nitrogen trap. The trap was weighed to give a yield of volatiles. The ¹H NMR spectrum of this liquid showed that it contained only toluene. When this procedure was compared with the extraction/standard analysis (vide supra) results were the same within experimental error.

The non-volatile residue was weighed and analyzed by TLC, showing one spot in benzene (Rf 0.25) which exhibited a characteristic mercury vapor emission when developed under UV light. A mass spectrum of the same sample showed a characteristic R₂Hg⁺ pattern and fragmentation peaks (R⁺, R₂Hg⁺, R₂Hg⁺). The ¹H NMR δ 2.04 (4, s, —CH₃HgCH₂—, J₃CH = 137 Hz), 7.01 (10, m, C₆H₅). All evidence points to dibenzylmercury as the sole nonvolatile product.

Product Analysis in the Low Potential Electroreduction of 2. The electroreduction of 2 at strongly cathodic potentials was described previously. When the working potential for the reduction was more positive (>−1.20 V) there appeared new signals in the NMR spectrum of the reaction mixture, and the isolated products exhibited a characteristic mercury vapor emission on TLC development under UV light. Electroreduction was performed in the same manner as the reduction of 2
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eXcept that the cold trap was replaced by a drying tube. Products were extracted with ether as described previously for the high potential reduction of $2^1$. Removal of solvent was done either by fractional distillation using Vigreax columns or by evaporation in poor vacuum (100—150 torr). The two different methods in the product isolation did not change the observed product composition.

Ethereal extracts were examined by GLPC prior to evaporation as well as the liquid residue after the removal of solvent. The ratios between the peak areas corresponding to the reduction products were the same in chromatograms obtained by both methods. Identity of signals were established by the comparison with authentic samples. $^1$H NMR of the crude product showed phenylcyclopropane (8); $\delta$ 0.4—1.0 (4, m, cyclopropyl-$\text{CH}_2$) 1.5—2.0 (1, m, cyclopropyl-$\text{CH}$) 6.9—7.4 (5, m, $\text{C}_6\text{H}_5$). From the integral area the relative percent of phenylcyclopropane was calculated.

The reaction product was washed twice with 40 mL portions of pentane. The white pentane insoluble residue was recrystallized from $\text{CCl}_4$ (34% isolated after two recrystallizations, mp 92—93°C). NMR $\delta$ 2.7 (2, m, $-\text{CH}_2$) 3.6 (3, m, $-\text{CHHg}$, $-\text{CH}_2$) 7.2 (5, m, $\text{C}_6\text{H}_5$); TLC (hexane) Rf 0.03) of material than exhibited mercury vapors upon development under UV light. The mass spectrum showed a set of peaks with characteristic mercury isotope natural abundance patterns; m/e 474—482 ($\text{C}_8\text{H}_{16}\text{HgBr}_2$), 356—364 (HgBr$^+$), 277—285 (HgBr$^+$) and other peaks for $\text{C}_8\text{H}_9\text{Hg}^+$, $\text{C}_8\text{H}_5\text{Hg}^+$, and $\text{C}_8\text{H}_5\text{Hg}^+$.

A sample of this material in $\text{CCl}_4$ consumed bromine rapidly to give 1,3-dibromo-1-phenylpropene (2) as the only organic product, and a white solid found to be HgBr$_2$. These results identify the pentane insoluble solid product as 1.

The pentane extract, upon evaporation of solvent, gave a viscous yellow liquid which showed two spots on TLC (benzene; ethyl acetate 9:1), Rf 0.61 which showed mercury upon development with a UV lamp, and Rf 0.68 which was mercury free. The mixture could not be separated on preparative TLC, but an NMR of the mixture showed phenylcyclopropane to be present, and additional peaks at $\delta$ 1.25, 3.0—3.5, 4.2 (m) and 7.0—7.3.

Treatment of a small sample of this material with LiAlH$_4$ in ether rapidly gave droplets of mercury. GLPC analysis of the reduction mixture showed that phenylcyclopropane and 3-bromo-1-phenylpropene (9) were present. GLPC of the original pentane extract (120°C, 8 ft. DEGS column) showed two peaks, phenylcyclopropane (8) (40%) and another compound (60%) with a retention volume 9.5 times that of 8. This material was collected from preparative GLPC as a pale yellow liquid mixed with black droplets. The mass spectrum of the liquid, m/e 238 ($\text{C}_{18}\text{H}_{22}$) corresponded to that of 2,3-diphenylhexane. From these data it was concluded that the pentane soluble fraction consisted of a mixture of 8 and 11.

Product Analysis in the Electroreduction of 9. Reductions of 9 were carried out at $-2.15$ V or $-2.50$ V in DMF with 0.2 M Et$_4$BF$_4$ (Et$_4$BF$_4$ = 2.25 V, DMF, 0.02 M Et$_4$NF$_4$). Samples taken from the reaction mixture during reaction showed, upon TLC (hexane), characteristic mercury vapor for one spot (Rf 0.22) but not for the second spot (Rf 0.48). The second spot corresponded to authentic phenylpropene (14). The final reaction mixture was diluted with water and extracted with several portions of ether. The ether was washed with water and dried over anhydrous sodium sulfate. Removal of the ether by distillation through a Vigreax column gave a semisolid which by both NMR and GLPC could be shown to contain 1-phenylpropane and one other compound. NMR of 14; $\delta$ 3.78 (3, m; $-\text{CH}$) 1.5 (2, m, $-\text{CH}_2$) 3.5 (2, t, $-\text{CHAr}$) 7.1 (5, m, $\text{C}_6\text{H}_5$); NMR of second compound; $\delta$ 0.75 (2, t, $-\text{CH}_2\text{Hg}$), 2.05 (2, m, $-\text{CH}_2$), 2.86 (2, m, $-\text{CH}_2\text{Ar}$) 7.1 (5, m, $\text{C}_6\text{H}_5$). Mass spectrum of the mixture gave a characteristic mercury (Hg$^+$) pattern at m/e 196—204 (except 197, 203), but no parent peak could be found. Bromanization of the reaction mixture dissolved in $\text{CCl}_4$ gave a mixture of 1-bromo-3-phenylpropane (9) and 1-bromo-1-phenylpropane. Identity of the samples was verified by GLPC against authentic samples. If the original semisolid residue were pumped in vacuum for an extended period and distilled (bp 78°C, 0.03 torr) an oil was obtained which exhibited the NMR characteristics cited above, gave only 1-bromo-3-phenylpropane on treatment with a deficient amount of bromine in $\text{CCl}_4$, and gave a single mercury containing compound on TLC in hexane (Rf 0.23). From these data it was concluded that the organomercurial obtained was 15.
Acknowledgement. — Acknowledgment is expressed to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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SAZETAK

Elektroorganska kemija. VII. Uloga živa(I)-soli u elektroredukciji benzilbromida

M. Tarle, O. Rasmy, H. Rogers i J. Casanova

Elektroredukcijom na živinoj katodi različitih benzilmono- i 1,3-dibromida i benzilživa(I)-halida dobiveni su produkti koji potvrđuju da u mehanizmu elektroredukcije bromida sudjeluju organoživa(I)-spojevi i vjerojatno živa(I)-dimeri. Pro- dukti koji su nastali ukazuju da monomolekulske u odnosu na bimolekulske reakcije adsorbiranih organoživa(I)-spojeva ili dimera jako ovise o prisustvu j ako adsor- biranih elektroneaktivnih tvari i da prisutnost takvih površinski aktivnih tvari može u nekim slučajevima omogućiti nastajanje novih produkata, što je važno za vođenje elektroorganskih sinteza.