CROATICA CHEMICA ACTA CCACAA 63 (2) 225—238 (1990)

CCA-1938

YU ISSN 0011-1643
UDC 541.13
Original Scientific Paper

Electroorganic Chemistry. VI.[1] Mechanism and Product Studies in the Electroreductoin of 1,3-Dibromides

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Received September 12, 1989

Products of the electroreduction of 1,3-dibromopropane, 1,3-dibromo-1-phenylpropane, 1,3-dibromo-1,3-diphenylpropane, *endo*-4-syn-8-dibromodibenzobicyclo[3.2.1]octadiene, and 1,8-bis-(bromomethyl)naphthalene at a mercury cathode were examined. The influence of change in potential, of addition of radical and carbanion scavengers, of added adsorbable species on product distribution, and the presence of organomercurial species in the products implicate a reaction path which involves sequential one electron reductions with the intervention of organomercury(I) radicals and possible dimeric mercury(I) species.

INTRODUCTION

During the investigation of the electrochemical behavior of vicinal dibromides[2] and 1,ω-dibromides[3] on a mercury electrode, our attention was drawn to the electroreduction of 1,3-dibromides, which has been a subject of investigations during the past two decades. Polarographic analyses of 1,3-dibromopropane (*1*) carried out by Zavada and coworkers[4] led to speculations that a slow two-electron reduction process preceeded a fast intramolecular cyclization. Their opinion clearly included a concerted ring closure.

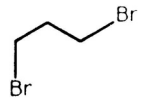
Rifi reported that electroreduction of dibromides was a useful general synthetic method for the preparation of higly strained small ring compounds.[5,6,7] It was argued that the halfwave potential observed in the reduction of *1*[4] is less cathodic in comparison with those of monobromides[8] due to the inductive effect of the neighboring carbon-bromine bond, and the lower activation energy of the transition state.[6] Consequently, a concerted reaction mechanism for the electroreduction of *1* did not divert product from the formation of exclusively cyclopropane.

Gerdil observed two distinct waves in voltammograms of both benzyl bromide (*2*) and 1-phenyl-1,3-dibromopropane (*3*).[9] The first wave was attributed to the formation of carbon free radicals and the second to their further reduction. The half-wave potentials of *3* were shifted toward more anodic values in comparison with those of *2*. According to Gerdil this phenomenon was caused by the assistance of the nonbenylic C—Br bond electrons in the electrode reduction steps.

Fry and Britton showed the electroreduction of stereoisomeric 2,4-dibromopentanes is a stepwise process proceeding via intramolecular cyclization.[10] Transient intermediates leading to the straight chain product (pentane) and secondary reduction products (2-pentene and 3-pentene) were detected by GLPC. They found that both *d,l*- and *meso*-2,4-dibromopentane give approximately the same amount of *cis*- and *trans*-1,2-dimethylpropane, suggesting a stepwise mechanism for their formation.

Reduction of *endo*-2-*endo*-6-dibromobornane in the absence of controlled potential on a mercury electrode gave tricyclene and bornane.[11] Grimshaw speculated that carbanionic cyclization and competitive diradical coupling led to the formation of tricyclene, excluding the intervention of organomercuric radical intermediates.

Wiberg reported that the electroreduction of *1* yields on a platinum cathode a mixture of propane (*4*) and cyclopropane (*5*).[12] Propane was obtained as a major product at low working potentials. Intermediate organic radicals were



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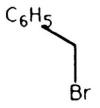

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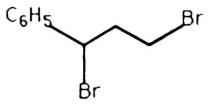

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successfully intercepted by means of benzylmethyl ether (*6*), which acted as a hydrogen atom donor. On the basis of voltammetric experiments carried out on a mercury-coated platinum electrode, the formation of organomercuric intermediates in this reaction was ruled out.

RESULTS AND DISCUSSION

With this background of seemingly contradictory evidence, we undertook a product study of the electroreduction of 1,3-dibromides. The product composition dependence on the stability of intermediates, geometry of substrate and thermodynamic stability of products were examined. In our hands electroreduction of *1* on a stirred mercury cathode by either controlled potential electrolysis (cpe) or controlled current electrolysis (cce) yielded cyclopropane nearly quantitatively (Table I). Addition of water to the solvent did

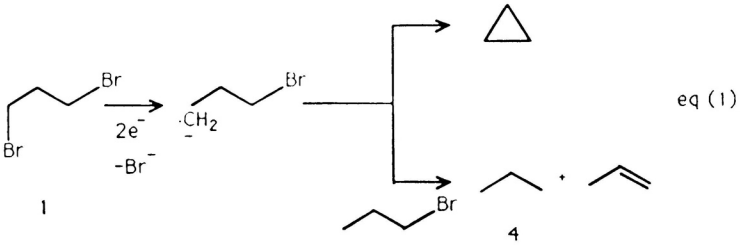
TABLE I

Products of the Electroreduction of 1,3-dibromo-1-phenylpropane (3)

Potential V vs. sce	Solvent	Trapping agent	PRODUCTS, %[a] *8*	*9*
—2.10	DMF[b]	—	100	—
—2.10	80% AcOH[c]	—	27	73
—1.70	DMF[b]	Ph_3CH[d]	77	23

[a] Relative percent of all total yield were in excess of 85%.
[b] 0.2 M Et_4NBF_4 as supporting electrolyte.
[c] 0.2 M AcONa as supporting electrolyte.
[d] The ratio of Ph_3CH to substrate was 1.2 to 1.

not result in a significant change in the product ratio as reported by Rifi.[5] It had been demonstrated that water is a rather poor proton donor due to the high degree of structure in water/dimethylformamide (DMF) solution.[13] Weaker association between methanol and DMF results in a stronger specific adsorption of the alcohol on a cathode, increasing the proton donating ability of this reagent in the Helmholtz layer. The reduction of *1* yielded a small but reproducible amount of propane in DMF-methanol and DMF-methanol--water, suggesting the interception of a intermediate carbanion. That suggestion was supported by the result of electrolysis of *1* in acetic acid. Using pure acetic acid as the proton source, we found 7% propane. Although propane was formed in low yields, the results suggest the presence of a short--lived, carbanion intermediate which was partitioned between the ring closed (S_N2) product and proton capture (eq. 1);

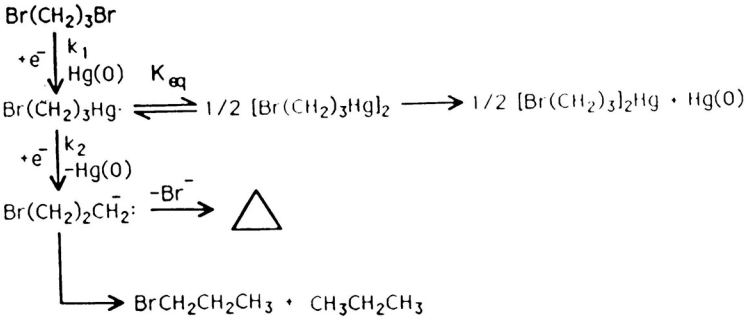


eq (1)

At the high potentials employed, 1-bromopropane would be reduced to propane (*4*). The 1-bromopropane may also serve as a proton source in an E_2 process, leading to the propene observed in the absence of protonic solvents. Chronoamperograms measured during the electroreduction of *1* were of the nonexponential ECE type.[1,3,14] This result suggests a stepwise rather than concerted two-electron transfer. The ECE curve shape required the separation of two electrochemical steps by an intervening slower chemical step. It would not be observed if the reduction of *1* involved a concerted two-electron mechanism to form a carbanion. The isolation of a very small amount ($< 1\%$) of di-*n*-propylmercury from the catholyte during the electroreduction of *1* takes on special significance in the light of this observation.

Organomercurials have been identified previously in the electroreduction of bromides,[3] and organomercury(I) radicals are known to be precursors of organomercurials.[15] We propose that the observed ECE behavior is linked to the intermediacy of $RHg^{\cdot}$, organomercury (I) radicals and their dimers.[1] The behavior observed at a mercury cathode is unlike that reported by Wiberg and Epling[12] for the reduction of 1,3-dibromopropane at a platinum cathode. However, in the present case addition of benzylmethyl ether (*6*) to the catholyte did not change the reaction products at all, even at a very low potential. Therefore, the formation of free organic radicals during the electroreduction of *1* is not indicated. This is consistent with the general observation that organic radical coupling products are found rarely in the high potential reduction of halides on a mercury electrode.

The dimerization of RHg· on the electrode surface may be part of the chemical step observed indirectly from chronoamperometric curves. The shape of the chronoamperometric curve suggests that the ratio between the electrochemical rate constants is $k_2 > k_1$ and the magnitude of the equilibrium constant ($K_{eq} \gg 1$) for the radical coupling process. Consistent with these observations, we suggest an overall reduction mechanism similar to one previously proposed (Scheme 1).[1,3,17] For the electroreduction of 1,ω-dibromides, we earlier proposed that unstable mercury(I) dimer remains on



Scheme 1

the mercury surface during the symmetrization process,[3] due to the presence of the remaining terminal C-Br bond which is strongly adsorbed on the electrode surface. It is possible that the intermediate formed in the electroreduction of *1* behaves in a similar manner. If true, dialkylmercury could be formed by the further reduction of the radical intermediate, while it is still adsorbed on the cathode. However, electroreduction of *1* and other 1,3-dibromides in the presence of anthracene yielded cyclic products almost exclusively. In contrast, reduction of numerous monobromides and higher 1,ω-dibromides gives anthracene adducts under the same circumstances. These results support carbanionic intramolecular cyclization in the reduction of 1,3-dibromides.

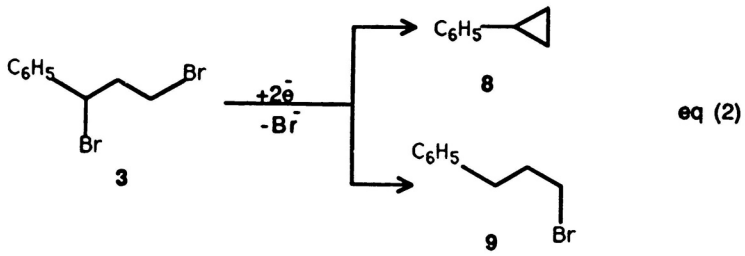
Useful mechanistic information was derived from the electroreduction of *1*, but limited stability of the reaction intermediates was a barrier to a more detailed analysis. Hence, electroreduction of 1,3-dibromo-1-phenylpropane (*3*) vas carried out. Inasmuch as the half-wave potentials for the benzylic carbon-bromine bond ($E^1_{1/2}$ —0.29 V, $E^2_{1/2}$ —0.86 V, $E^3_{1/2}$ 1.26)[19] and nonbenzylic C-Br bond ($E^4_{1/2}$ —2.12 V) of *3* differed substantially, the working potential in the exhaustive electrolysis was chosen to be close to $E^3_{1/2}$. In an aprotic solvent, such as DMF, phenylcyclopropane (*8*) was observed (Table II). With an increase in the proton donating strength of the solvent (eg., methanol, water), 1-bromo-3-phenylpropane (*9*) was found to be present in a small amount. Increasing the acidity of the solvent even further increased the amount of *9*. These results are best rationalized by the formation of an intermediate long-lived, resonance stabilized carbanion which survives for

TABLE II
Products from the Electroreduction of 1,3-dibromo-1-Phenypropane (3) at -0,85 V

Solvent	Supporting electrolyte[a]	Trapping agent[b]	Yield, %[c]	n	PRODUTS, %		
					8	*9*	*26*[d]
DMF	Et_4NBF_4	none	68	1.01	24	40	36
DMF	Et_4NBF_4	$PhCH_2OCH_3$	62	1.19	40	40	20
DMF	$LiClO_4$	none	61	1.28	51	41	8

[a] 0.2 M cocentration.
[b] Substrate to trapping agent ratio 1:1.2.
[c] Based on equivalents of substrate.
[d] Organomercurial described in the accompaning and following paper.

a longer time than the bromocarbanion from the reduction of 1, and thus would be more easily intercepted in acidic solvents (eq. 2).



eq (2)

Experiments were carried out in the presence of the free radical scavengers benzylmethyl ether (*6*) and triphenylmethane (7) (Table II). These compounds did not alter the product composition significantly, giving only 1.6% of phenylpropane (*10*). This is further suggestion that carbon free radicals may not be involved in the reduction of *3* at a mercury cathode. Organomercurials (26) were not found in the reaction products of *3* at high reduction potentials. However, they were the major products at the potentials below $E^3_{1/2}$.

Product analyses and shape of the chronoamperogram of *3* were similar to those observed in the electroreduction of *1*, and suggested that an organomercury radical was the reduction intermediate even at high potentials. The specific adsorption on the mercury cathode of polarizable functional groups, such as the phenyl ring, may play a crucial role in product determining steps.[20] The presence of passive polarizable functional groups could prevent the rapid desorption of the organomercuric radical and lead to more efficient coupling or reduction of RHg· to carbanion. Reduction of RHg· may be responsible for the absence of organomercurials among the products of reduction of *3* at high potentials.

We investigated the electroreductive behavior of 1,3-dibromo-1,3-diphenylpropane (*11*) at a potential above $E^2_{1/2}$ ($E^1_{1/2}$ —0.29 V, $E^2_{1/2}$ —0.91 V) and at moderate concentration of substrate. Under these conditions, it yielded no 1,3-diphenylpropane (*13*), but gave 1,2-diphenylcyclopropane (*12*) as the only products regardless of the proton donating ability of the solvent (Table III). Using benzylmethyl ether or triphenylmethane as radical scavengers, reduction of *11* did not yield 1,3-diphenylpropane in the potential range

TABLE III

Electroreduction of 1,3-dibromo-1,3-diphenylpropane[a] *(6) at -0.85 V*

Solvent	Supporting electrolyte[b]	Conc. (M)	Trapping agent[e]	Yield, %	n	Products %[c,d] *12*[c]	*12*[t]
DMF	Et_4NBF_4	0.092	none	91	2.01	22.5	74.5
DMF	Et_4NBF_4	0.084	$PhCH_2OCH_3$	94	1.06	30.5	67.8
DMF	Et_4NBF_4	0.073	Ph_3CH	61	1.99	20.0	77.0
AcOH[f]	NaOAc	0.093	none	90	—[g]	45.2	54.8

[a] d,l: meso ratio 59:41.
[b] 0.2 M concentration.
[c] Relative percent.
[d] One to three percent of weight of an unidentified organomercurial was found in these cases.
[e] Substrate to traping agent ratio was 1:1.2.
[f] 80% aqueous.
[g] Not meaningfull. solvent was extensively reduced.

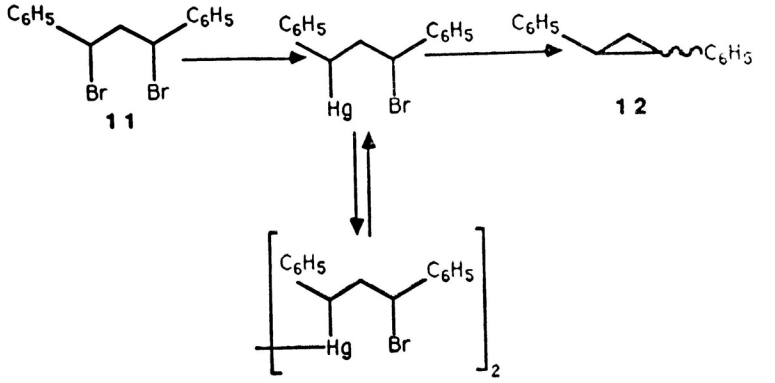
TABLE IV

Electroreduction of 1,3-dibromo-1,3-diphenylpropane[a] *(6) at high potentials*

Solvent[b] V	Potetial M	Conc.	Trapping Agent	Yield	n	Products, %[c] *12*[c]	*12*[t]	*13*
DMF	—1.30	0.057	none	81	2.01	50.0	50.0	8.6
DMF	—2.15	0.087	none	87	1.96	48.7	51.3	10.0
DMF	—2.15	0.020	none	71	2.08	39.2	50.8	14.0
DMF	—2.15	0.008	none	08	2.31	40.0	46.0	

[a] d,l: meso ratio 59:11.
[b] 0.2 M cocentration of Et_4NBF_4.
[c] Relative percent.

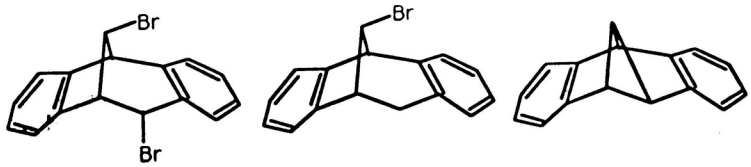
—1.00 V to —1.30 V. Reduction of *11* at —0.85 V gives small but reproducible amounts of the compound which we believe to be a dialkylmercurial. This observation suggests that mercuric radicals are also precursors of the stable products in the electroreduction of *11*. Gas chromatographic analysis showed that no volatile final products were formed until the electron consumption had reached 45% of the total theoretically required for a 2-electron reduction (Table IV). A mixture of stereoisomeric 1,2-diphenylcyclopropanes (*12c, 12t*) was the almost exclusive product. This result is not unexpected if the starting dibromide *11* and subsequent intermediates remain strongly adsorbed on the electrode surface. Indeed, the addition of aqueous acetic acid failed to alter the yield of cyclopropane products by intercepting a carbanion. These data may be rationalized by a stepwise process for 2 one-electron transfers in which the greater rate constant is associated with the first electron-consuming process. In support of that observation was the chronoamperometric curve shape for the electroreduction of *11*. Dibenzylic substrate *11* shows only two waves ($E^1_{1/2}$ —0.29 V, $E^2_{1/2}$ —0.91 V). Scheme 2 illustrates a mechanism which is consistent with these observations:



SCHEME 2

Such a scheme will satisfy our observations if the mercury(I) dimer is strongly adsorbed and reduced slowly at operating potentials. 1,3-Diphenylpropane (*13*) is formed, although in a small amount, even at lower potential (—1.00 V), but only in a dilute solution. Addition of benzylmethyl ether to the catholyte does not change the amount of *13* formed, suggesting once more that carbon radicals are not involved as intermediates. In agreement with this is the observation of an 11-fold increase in 1,3-diphenylpropane with the increasing potential (—1.60 V) and/or proton donating ability of the solvent (CH_3CO_2H) but maintaining low concentration of the substrate. These latter experiments suggest that the intermediate can be reduced further and captured. The stereochemical behavior of *11* is complicated with respect to potential and concentration dependence. This behavior will be discussed in a subsequent paper.

Electroreduction of *endo*-4-*syn*-8-dibromodibenzotricyclo[3.2.1]octadiene (*14*) was examined. Dibromide *14* has the carbon skeleton of *3* incorporated in a



rigid bicyclic structure. The C_1-C_3 distances in *14* and *3* are estimated from models to be essentially the same (ca. 2.5 Å), but the torsional angle between C-Br bonds is constrained in *14* and make ring closure more difficult. In addition, products derived from *14* and *3* would not be equally stable. Electroreduction of *14* at moderate potentials ($E^1_{1/2}$ —1.20 V, $E^2_{1/2}$ —2.42 V) gave monobromide *15* as a major product on either a mercury or carbon cathode (Table V). The smaller amount of dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (*16*) formed in the electroreduction of *14*, compared with that of phenylcyclopropane in the electroreduction of *3* indicates that strain in the ring closed

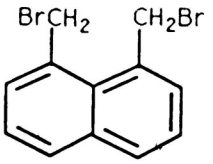
TABLE V

Electroreduction of 1-bromo-3-phenylpropane[a] *(9)*

Potential, V	Trapping agent[b]	Yield (%)	n	PRODUCTS, %[c] *15*	*16*
—2.15	none	34	1.32	37	63
—2.15	$PhCH_2OCH_3$	71	1.84	60	40
—2.15	Ph_3CH	59	1.77	59	41
—2.15	CH_3OH	62	1.80	70	30
—2.50	none	65	1.65	72	28
—2.50	$PhCH_2OCH_3$	72	1.84	79	21
—2.50	Ph_3CH	59	1.77	80	20
—2.50	anthracene	62	—	85	15

[a] All reactions were in DMF using 0.2 M Et_4NBF_4 as supporting electrolyte.
[b] Substrate to trapping agent ratio was 1:1.2.
[c] Relative percent. Yields were between 75 and 90%.

product is a critical factor in the product determining step. The importance of steric and geometric factors in product formation is further illustrated in the electroreduction of 1,8-*bis*(bromomethyl)naphthalene (*17*).



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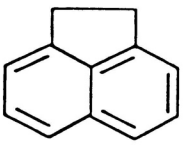

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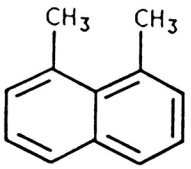

19

Approximately equal amounts of acenaphthalene (*18*) and 1,8-dimethylnapthalene (*19*) were obtained. Polarograms of *17* shows three waves ($E^1_{1/2}$ —0.20 V, $E^2_{1/2}$ —1.21 V, $E^3_{1/2}$ —1.42 V), indicating, as before, the possible formation of alkylmercuric salt and its further reduction to the stable products. Chronoamperograms were of the ECE type, and were consistent with previous mechanistic proposals.[1,3]

The geometry of *17* does not impose special restrictions on the orientation of the C-Br bond in the ground state, as was the case in the reduction of *14*. However, the cyclopentane ring in *18*, with the shorter C_9—C_{10} bond distance than in the parent compound (*17*), causes the substantial ring strain in the product in comparison to *19*. Once more the potential energy content of products seems an important factor in the product determining step.

The data from this study cannot be rationalized in the relatively simple ways suggested earlier.[6,9,10,11] Undoubtedly, electroreduction of 1,3-dibromides at mercury proceeds *via* a carbanion as the terminal reaction intermediate.[10] We find no evidence for either concerted reaction or carbon free radicals coupling cyclization. However, prior to the carbanion formation on a mercury electrode several processes, electrocatalytic and electroreductive can take place. These processes have a strong influence on the nature of the products, and the kinetics of their formation. Adsorbable functional groups seem to play

a crucial role in the overall process, promoting formation of organomercurials. Reactive benzylic carbon-bromine bonds undergoes electrocatalyzed chemical reaction, yielding organomercuric salts.[17,19] Not only is the electrocatalytic process potential dependent, but all the other consecutive steps in elecroreduction are markedly influenced by the reduction potential. Indeed, an anodic shift of the working potential in many cases completely changes the product composition yielding organomercurials as major products. The role of organomercuric salts in the electroreduction of the carbon-bromine bond is in itself an interesting one, and will be explored in a separate paper.

EXPERIMENTAL

General. Melting points and boiling points are uncorrected. ^{1}H NMR spectra were obtained with a Varian EM 390 spectrometer using carbon tetrachloride solutions with internal tetramethylsilane and in $CDCl_3$ solutions using a Brucker HX-90E spectrometer. Analytical GLPC was performed using an 8 foot Porapak Q column for gases at 80 °C. Liquids were analyzed on an 8 foot carbowax 20M column, 15%, using a Varian 90P chromatograph. The mass spectral data came from a Varian/MAT CH-5 mass spectrometer.

Mercury was Bethelhem grade, recycled as was described previously.[2] Reagent grade acetic acid and methanol were used as solvents, and dimethylformamide was purified prior to use.[2] Tetraethylammonium fluoroborate (Southwest Analytical Chemicals), anhydrous lithium perchlorate (Alfa Inorganics, Ventron) and anhydrous sodium acetate (Baker Chemical Co.) were commercial and were used without further purification. Tetra-*n*-butylammonium fluoroborate was prepared from tetra-*n*-butylammonium hydrogen sulfate (Aldrich Chemical Co.) and sodium fluoroborate (Alfa Chemicals, Ventron). All other chemicals used were reagent grade.

1,3-Dibromopropane (1). (Matheson, Coleman and Bell Co.) was used without further purification after it was shown to be of > 99% purity by GLPC analysis the carbowax column at 100 °C.

1-Bromo-3-Phenyl-2-propene (20).[22] Into an ice cooled solution of 15.19 g (113.3 mmol) of cinnamyl alcohol in 80 mL CCl_4, HBr gas was added for 5 hours. After addition of 200 mL of ether, the resulting solution was washed with water until neutral. Drying over anhydrous $MgSO_4$, filtration and removal of the solvent *in vacuo* gave a yellowish oil (21.1 g, 96%) which solidified at + 6° : ^{1}H NMR δ 3.95 (2, d, $-CH_2Br$), 6.13 (1, m, β-vinyl), 6.18 (1, d, α-vinyl), 7.13 (5, s, $-C_6H_5$).

1,3-Dibromo-1-phenylpropane (3).[23] In 50 mL of glacial acetic acid containing 21 g (106 mmol) of *20*, HBr gas was bubbled at 0 °C until saturation was achived. After the reaction mixture had stood for 60 hours at 0 °C, 200 mL of pentane and the same amount of water were added. The mixture was washed with 8 to 10 small portions of cold water. The organic solution was dried over $MgSO_4$, filtered and concentrated. The residual oil was distilled to give 25.5 g of colorless liquid 87%, bp 91 °C (1 mm); ^{1}H NMR δ 2.48 (2, m, $-CH_2-$), 3.20 (2, m, $-CH_2Br$), 5.08 (1, m, $-CHBr-$), 7.22 (5, s, $-C_6H_5$).

trans *-Benzalacetophenone* (21).[20] To an ice cold mixture of 10% aqueous sodium hydroxide (50 mL) and acetophenone (12 g, 100 mmol) in 95% ethanol was added (30 mL) benzaldehyde (10.6 g, 100 mmol) with stirring. After two hours standing at room temperature, crystallization was induced in the reaction mixture by cooling and scratching the flask. From the ice-cold slurry crystals were collected and washed with cold water and ethanol. The product was recrystallized from absolute ethanol using 5 mL of the solvent per gram of crystals. A pale yellow product was obtained (5.1 g, 48%, mp 56—58 °); ^{1}H NMR δ 7.95 (2, m, vinyl), 7.42 (10, m, $-C_6H_5$).

1-Bromo-1,3-diphenylpropan-3-one (22).[25] Into a solution of 5.05 g (24.2 mmol) of *21* in 30 mL of benzene, HBr gas was bubbled at 0 °C for 30 minutes. The yellow crystals which formed were collected and washed on a Buchner funnel with cold benzene until nearly colorless. After drying *in vacuo* for 2 hours, 4.76 g of a white crystalline material was obtained (68.2%, mp 104—105 °C): ^{1}H NMR

δ 3.89 (2, m, $-CH_2-$), 5.63 (1, t, $-CHBr-$), 7.40 (10, m, $-C_6H_5$); IR: 1690 cm^{-1} (C=O stretch).

1-Bromo-1,3-diphenylpropan-3-ol (23). To the ice cold slurry containing 38.5 g (133 mmol) of *22* in 1400 mL of methanol, the solution of 13.5 g (357 mmol) of sodium borohydride and 15 g of sodium methoxide in 450 mL of methanol was added in 14 portions. Reactant *22* slowly disssolved during 3 hours under stirring. The solution was poured into 1 liter of ice water and 100 mL of concentrated hydrochloric acid was added. The reaction mixture was extracted twice with ether. The combined organic layers were washed five times with cold water and dried over anhydrous $MgSO_4$. Removal of the solvent resulted in 27.85 g of a colorless viscous oil, 67.6%: ^1H NMR δ 2.32 (2, m, $-CH_2-$), 3.15 (1, s, —OH), 4.36 (1, m, —CHOH), 4.85 (1, m, —CHBr—, *meso*), 5.18 (1, m, —CHBr— *d, l*), 7.17 (10, m, $-C_6H_5$): IR 3650 cm^{-1} (—OH stretch). The product was converted to the desired dibromide *11* without further purification.

1,3-Diphenyl-1,3-dibromopropane (11) Gaseous HBr was bubbled for 190 minutes into an ice cold solution of 27.5 g (94 mmol) of *23* in 220 mL of CCl_4. The solution was stirred for one hour longer. After addition of ether (200 mL), the reaction mixture was washer with water until neutral. The solution was dried overnight ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave 33.7 g (99%) of a slightly yellow viscous oil. Molecular distillation resulted in 33.1 g (120 —124 °C at 0.04 μ), of a viscous oil which solidifed at + 6°C: ^1H MNR δ 2.82 (2, m, $-CH_2$), 4.79 (1/2, t, —CHBr—, *meso*), 5.12 (1/2, t —CHBr—, *d, l*), 7.21 (10, s, $-C_5H_6$).[26] From the integral ratio the isomer composition could be calculated; *d, l* : *meso* = 51 : 49.

The same diastereoisomeric mixture of *11* could also be synthesized by the action of bromine on the reaction mixture containing *cis* and *trans 12*.[27] To the isomeric mixture of 12 (1.1 g) in CCl_4 (40 mL), bromine (1.0 g, 0.35 mL) in CCl_4 (11 mL) was added dropwise. Immediate decolorization was observed. The mixture was stirred for 115 hours at room temperature. Evaporation of the solvent gave a brownish oil together with yellowish solid. Hexane (10 mL) was added, and the solid was removed by filtration. The clear residual solution was evaporated and the process was repead three times. The ^1H MNR spectrum of the isolated slightly yellow oil was identical with the spectrum of *11*.

trans-*7,8-Dichlorodibenzobicyclo[2.2.2]2.5-octadiene* (24).[28] In a thick-walled high pressure glass reactor tube were placed 1.25 g (7.2 mmol) of anthracene and 5 mL (6.28 g, 64.7 mmol) of *trans*- dichloroethene. The tube was evacuated and sealed after degassing. Six such tubes were heated for 24 hours at 200—205 °C, allowed to cool o room temperature, and the contents were transferred to a three-necked flask. A volatile material was removed by distillation. Maleic anhydride (10 g) and 180 mL of *m*-xylene were added to the solid residue and the resulting mixture was refluxed for one hour. After addition of 20 g of $NaHCO_3$, the *m*-xylene was removed by steam distillation, which was continued 90 minutes after the last trace of the volatile component had distilled. The reaction mixture was extracted with benzene and washed with water several times. Solvent was removed under reduced pressure and crude product was chromatographed on an alumina column (neutral, Brockman (activity grade 1) 80—200 mesh, Fisher Scientific Co.) using CCl_4 as an eluent. After recrystallization from absolute ethanol 9.16 g (76.8%, mp 112—114 °C) was obtained: ^1H NMR δ 4.18 (2, m, bridge), 4.40 (2, m, bridgehead), 7.29 (8, m, $-C_6H_4$).

Dibenzobicyclo[2.2.2]2.3.7-octatriene (25).[29] In 90 mL of diglyme, freshly distilled from $LiAlH_4$, 5 g (18.2 mmol) of *24* was dissolved and heated to reflux. Metallic sodium (1 g, 43.4 mmol) was added in small pieces over a 10 minute period. The solution turned dark, and was refluxed for 13 hours. Any unreacted sodium was destroyed by the addition of methanol (20 mL). The reaction mixture, diluted with 150 mL benzene, was washed witl water ten times and dried over anhydrous $MgSO_4$. After filtration and evaporation of solvent in vacuo, the product was chromatographed on alumina using CCl_4. The crude product was recrystallized from absolute ethanol yielding 3.09 g (84%, mp 118—119 °C) of white crystals: ^1H NMR δ 5.11 (2, m, bridgehead), 6.96 (6, m, aromatic and vinyl), 7.25 (4, m, $-C_6H_4$).

endo-4-syn-8-Dibromodibenzobicyclo[3.2.1]octadiene (14). Bicyclic dibromide *14* was prepared according to Cristol's synthesis of exo-4-syn-8-dichlorodibenzobicy-

clo[3.2.1]octadiene and its endo - chloro epimer.[30] To the solution of 1.0 g (5 mmol) of 25 in 20 mL of ethyl acetate, 1.44 g (0.5 mL, 9 mmol) of bromine in 10 mL of ethyl acetate was added. After standing for 4 hours, he reaction mixture was diluted with 100 mL of ether and the organic layer was washed twice with 10% aqueous $Na_2S_2O_3$ and then three times with water. The solution was dried over $MgSO_4$, filtered and the ether removed in vacuo, yielding a slightly yellow solid. Recrystallization of the solid from a mixture of 5 mL of ether and 16 mL of absolute ethanol gave 1.2 g of colorless crystals (3.3 mmol, 66%, mp 118.5—120 °C): NMR δ 3.70 (1, m, bridgehead), 3.96 (1, d, bridgehead), 4.80 (1, m, bridge —CHBr), 5.93 (1, d, α—CHBr, J = 4.5 Hz), 7.10 (7, m, aromatic), 7.40 (1, m, aromatic). Anal. Calcd. for $C_{16}H_6Br_2$: C, 52.78; H, 3.32. Found: C, 52.37; H, 3.47.

1,8-Bis(hydroxymethyl)naphthalene (25).[31] A slurry of 20 g of naphthalic anhydride, (100.0 mmole) in 50 mL of benzene was added slowly to a stirred suspension of lithium aluminum hydride (10 g., 263 mmol) in 200 mL of dry ether and 40 mL of benzene. The resulting solution was refluxed for four hours and ether was removed by distillation. The excess of $LiAlH_4$ was destroyed by careful addition of ethyl acetate. Precipitation with the 10% aqueous potassium hydroxide (20 mL) gave white solid which was extracted twice with a benzene-ether mixture. Evaporation of the combined extracts to 50 mL and addition of 50 mL of ethanol was followed by further evaporation to 40 mL. The product was obtained by the addition of aqueous sulfuric acid and filtration in vacuum. Recrystallization from absolute ethanol yielded 1.57 g of a white crystalline substance (8.8%, mp 154.5 °C: ^{1}H NMR δ 4.45 (2, t, —OH), 5.25 (4, d, —CH_2—), 7.3—8.0 (6, m, aromatic).

1,8-(Bisbromomethul)naphthalene (17).[31] To a stirred solution of 1.07 g (5.7 mmol) of *26* in benzene (36 mL) and ether (14 mL), phosphorus tribromide (1.07 g, 4 mmol) in ether (10 mL) was added over a 2 hour period. The mixture was refluxed for one additional hour and poured onto 200 mL of ice water. The organic layer was washed with cold aqueous $NaHCO_3$ and water. After drying over $MgSO_4$ and filtering, the solution was concentrated under reduced pressure. Recrystallization from ether gave 0.76 g (3.2 mmol, 56%) of white crystals, mp 129—130.5 °C: ^{1}H NMR δ 5.33 (4, s, —CH_2Br), 7.2—8.1 (6, m, aromatic).

1,8-Dimethylnaphthalene (19).[31] A solution of 0.2 g of *26* (0.85 mmol) in ether (20 mL) was added to the stirred solution of 50 mg of $LiAlH_4$ (1.3 mmol) in ether (20 mL) over 30 minutes. After stirring the reaction mixture overnight, the excess hydride was destroyed by the careful addition of water. The reaction mixture was washed with dilute hydrochloric acid and eight times with small amounts of water. The ethereal solution was dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was dissolved in absolute ethanol and the solution was cooled. The crystalline product was collected and dried in vacuo. The yield was 0.14 g (84%) mp 61—62 °C: ^{1}H NMR δ 2.67 (6, s, — CH_3), 7.1—7.7 (6H, m, aromatic).

Electrochemical Experiments. The electrochemical cell used in this work was essentially the same as that described previassly.[2] Constant potential was maintined by means of a PAR model 373 Potentiostat-Galvanostat, Princeton Applied Research Corp., Princeton, N. J. For the controlled current electrolyses a Power Designs Model 5015T Regulated DC Power Supply was used. Electrolyses were followed coulometrically with the current-time relationship recorded on Simpson Multicorder 605, Simpson Electric Co., Chicago, Ill., connected in series with the cell. Current yields were calculated from the integral of the current time curves and from a PAR Model 379 Digital Coulometer with IR compensation.

Product Analysis from Electroreduction of 1. During the electroreduction a constant stream of nitrogen was passed through the cell and the volatile produsts were collected in a trap at liquid nitrogen temperature. After completion of the electrolysis, the contents from the cold trap were pumped directly into a high vacuum line. The material was fractionated at a temperature suitable to separate the volatiles from the solvent, and amount of gaseous product was measured volumetrically. The gaseous products cyclopropane and propane were analyzed by GLPC and the identity of signals was determined by comparison with the authentic samples.

Nongaseous products were isolated from the catholyte, which was diluted with 100—150 mL of water and extracted twice with ether (100 mL). The combined ether layers were washed with water (5 × 100 mL) and dried over anhydrous

Na_2SO_4 or $MgSO_4$. After evaporation of the solvent *in vacuo*, the residue was examined by GLPC and analyzed by NMR. The isolated oily material showed one peak on a Carbowax 20M column with a different retention time when compared to other products, solvents, starting material or 1-bromopropane. The ^1H NMR spectrum of this material was similar to those of numerous organomercurials isolated as reduction products of 1,ω-dibromides[3]: ^1H NMR 3.53 (4, t, $—CH_2Br$), 2.36 (4, m, $—CH_2—$), 1.26 (4, m, $—CH_2—Hg$). Treatment of the liquid with a dilute solution of bromine in carbon tetrachloride yielded a white precipitate and a clear liquid. GLPC of the liquid phase showed only 1,3-dibromopropane, (identified by comparison to an authentic sample prepared by the reaction between bromine and dibromodialkylmercury.)[32] Consequently, the liquid product of the electroreduction of *1* was assigned as ω,ω'-dibromodipropylmercury.

Product Analysis in Electroreduction of 3. Electroreduction was performed in the same manner as the reduction of *1* except that the cold trap was replaced by a drying tube. Products were extracted with ether as described previously. Removal of solvent was done either by fractional distillation using a Vigreaux column or by evaporation in poor vacuum (100—150 torr). The two different methods used in the product isolation did not change the observed product composition.

Ether extracts prior to evaporation as well as the liquid residue after the removal of solvent were examined by GLPC. The ratios of 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.

^1H NMR of the isolated products were compared with the spectra of the commercial samples of candidate compounds and with spectra obtained from the synthetic mixtures of these samples. Synthetic mixtures were made in the ratio calculated from the GLPC analysis of the reduction products *3*. Phenylcyclopropane shows three sets of peaks in the ^1H NMR δ 0.7—0.8 (4, m, $—CH_2CH_2—$), 1.75 (1, m, ArCH—), 7.00 (5, m, C_6H_5),[33] while 1-bromo-3-phenylpropane exhibits different signals in the NMR: δ 1.98 (2, m, $—CH_2—$), 2.46 (2, m, $—CH_2Ar$), 3.16 (2, t, $—CH_2Br$), 7.11 (5, s, $—C_6H_5$). Phenylpropane was observed only in GLPC analysis (> 1% detectable) and its signals could not be seen in NMR spectra of the electrolysis product of *3*.

Product Analysis in the Electroreduction of 11. Electrolysis, isolation of products and product identification were the same as described for the product study in the reduction of *3*. *Cis-* and *trans*-diphenylcyclopropane, isolated as products in electroreduction of *11*, exhibited different retention times on a carbowax 20M (15%) GLPC column. The experiments were performed in the following way; over increments of time (see Table IV) 100 µl of catholyte were removed without interruption of the reaction progress. Samples were placed in vials immersed in a dry ice-acetone bath. Water (2 mL) and ether (1 mL) were added to each sample and the organic layer was examined by GLPC. For both *cis-* and *trans*-diphenylcychopropane resolution of peaks was excellent. Fifty milligrams of each isomer was isolated by preparative GLPC. Their ^1H NMR spectra were identical to those reported previously:[34] NMR; *cis- 12* δ (2, m, $—H_2—$) 2.41 (2, m, Ar*CH*—*CH*Ar), 6.95 (5, s, $—C_6H_5$); *trans- 12* δ (2, m, $—CH_2—$), 2.12 (2, m, Ar*CH*—*CH*Br), 7.11 (5, s, $—C_6H_5$). Mass spectra showed a molecular peak M^+ 194, and fragmentation pattern characteristic for aromatic ring cleavage.

1,3-diphenylpropane (*13*), on GLPC under the same conditions, gave t_R 560 sec. It was characterized by isolation from preparative GLPC and by determination of its ^1H NMR spectrum: δ 1.26 (2, m, $—CH_2—$), 2.79 (4, t, $—CH_2Ar$), 7.08 (10, s, $—C_6H_5$). The mass spectrum of *13* showed molecular peak M^+ 196.

The stability of reaction products, *cis-* and *trans- 12*, was demontrated by several experiments to determine whether *13* was the primary reaction product. The mixture of both isomers of *12* (*cis* : *trans* = 39.2 : 60.8) was placed in an electrochemical cell (DMF, 0.2M Et_4NBF_4) and the circuit through the cell was closed (—2.00 V) for 5 hours. Products were recovered in the manner described in the electrolysis of *11* and showed by GLPC a *cis* : *trans* ratio of 39 : 61. This ratio was not changed after storing of that sample at room temperature for 6 months.

No trace of *13* was present in the sample after the electrochemical experiment or after 6 months standing. Intramolecular interconversion of electrocatalytic diastereoisomeric *d, l* and *meso- 11* was ruled out on the basis of the following experiments: compound *11 d, l : meso* = 49 : 51, 50 mg) in z mL CCl_4 and a drop of mercury were placed in an NMR tube. Spectra taken at intervals of 1, 2, 4, 8, 24 and 48 hours did not show any change in the isomer mixture. The same observation was made when the above diastereoisomeric mixture of *11* was stirred for 16 hours in an open circuit electrochemical cell (DMF, 0.2M Et_4NBF_4).

Product analysis for the Electroreduction of 14. The reduction procedure and products workup were the same as those described previously for *3* and *11*. Reduction potential on the carbon cathode was chosen to produce a reasonable current (50 to 300 mA) by changing potential prior to the start of the main reduction. Half-wave potential data were not available for the carbon electrode. Separation of the reduction products by either fractional crystallization or sublimation failed, and the product composition was studied by NMR.

The ^1H NMR spectrum of products did not show a benzylic —CHBr signal. A peak corresponding to the bridge —CHBr— remained, although in a decreased magnitude *versus* aromatic protons (in comparison with the spectrum of *14*). From these data the percent of monobromide *15* in products was calculated; NMR for *15*; δ 2.33 (1, d, bridgehead), 3.31 (1, m, bridgehead), 3.91 (2, d, benzylic CH_2), 6.99 (8, s, aromatic). In the same spectrum, peaks corresponding to tricyclic hydrocarbon *16* were observed:[35] ^1H NMR δ 2.88 (2, d), 3.55 (1, m), 4.35 (1, d), 7.03 (8, m). The integral ratio of aromatic protons to cyclopropyl bridgehead protons (from *16*) at δ 2.88 gave the percent of the cyclization product *16* in the reduction mixture.

Following Cristol's procedure[36] for electrophilic ring opening of *16* by the addition of bromine, it was found that electroreduction products of *14* (185 mg) in ethyl acetate (75 mL) decolorized 0.025 mL of bromine in ethyl acetate (8 mL). After stirring the reaction mixture for 15 hours and evaporating the solvent, the NMR of the reaction products did not show any peaks characteristic for *16*, but signals were found corresponding to *trans*-4,6-dibromodibenzobicyclo[3.3.0]octadiene: δ 5.80 (1, d, C—6 H, bearing *anti*-bromine), 5.73 (1, d, C*H*—4, bearing syn-bromine); $J_{4,5} \doteq 7H_z$, $J_{5,6} = 3HZ$. Other peaks of the same substrate were superimposed on the signals of *15*.

Product analysis in electroreduction of 17. Electrolysis and work-up procedure were performed as described for other benzylic substrates: ^1H NMR δ 2.66 (s), 2.96 (s), 6.9—7.7 (m). The integral ratio between the first two signals was 12 : 10. That spectrum showed signals corresponding to 1,8-dimethylnaphthalene (*18*): NMR δ 2.64 (6, s, —CH_3, 7.1—7.7 (6, m, aromatic). An authentic sample of acenaphthalene (*18*) showed the following signals in the ^1H NMR: δ 2.95 (4, s, —CH_2CH_2—), 6.9—7.6 (6, m, aromatic). A synthetic mixture of *18 : 17* in the ratio 45 : 55 gave an NMR spectrum identical to that obtained from the electroreduction products of *17*.

Acknowledgement. Appreciation is expressed to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial partial support of this research.

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SAŽETAK

Elektroorganska kemija. VI. Istraživanja mehanizma i produkata elektroredukcije 1,3-dibromida

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Istraženi su produkti elektroredukcije na živinoj katodi 1,3-dibromopropana, 1,3-dibromo-1-fenilpropana, 1,3-dibromo-1,3-difenilpropana, *endo*-4-*sun*-8-dibromodibenzobiciklo 3.2.1 oktadiena i 1,8-*bis*(bromometil) naftalena. Utjecaj promjene potencijala, dodatka radikala i karbaniona, dodatka površinski aktivnih vrsta na razdiobu produkta i prisutnost organoživinih vrsta u produktima ukazuje da reakcije teku putem uzastopnih jednoelektronskih redukcija uz sudjelovanje organoživa(I)-radikala i, vjerojatno, dimernih spojeva žive(I).