E. Electrolysis of Dimethyl *o*-[Bis-β-ethoxycarbonylvinyl]-phenethylsulfonium *p*-Toluenesulfonate (XIV). Preparation of XIV. ***o*-2-Bromoethylbenzaldehyde**[40] was converted to its diethyl acetal, bp 101° (0.50 mm), $n^{23.5}_D$ 1.5180, in 85% yield using the triethyl orthoformate procedure.[41]

Anal. Calcd for $C_{13}H_{19}BrO_2$: C, 54.36; H, 6.66. Found: C, 54.60; H, 6.44.

A solution of 10 g (0.37 mole) of sodium hydroxide in 270 ml of ethanol was saturated with methyl mercaptan and heated for 1 hr under reflux[42] with 107.6 g (0.37 mole) of the above bromoacetal. After cooling, the mixture was filtered, the alcohol was removed from the filtrate by distillation at 40° (maximum), the residue was diluted with dry ether and filtered, and the filtrate was fractionated. There was collected at 105° (0.35 mm) to 106° (0.27 mm) 87.7 g (90.5%) of ***o*-2-methylthioethylbenzaldehyde diethyl acetal**, n^{24}_D 1.5170.

Anal. Calcd for $C_{14}H_{22}O_2S$: C, 66.09; H, 8.72. Found: C, 66.14; H, 8.93.

The thioacetal (87.7 g) was hydrolyzed by refluxing with dilute sulfuric acid to 57.4 g (92.2%) of ***o*-2-methylthioethylbenzaldehyde**, bp 95° (0.40 mm), $n^{23.5}_D$ 1.5782.

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.62; H, 6.71. Found: C, 66.27; H, 6.46.

A solution of 57.4 g (0.32 mole) of the aldehyde, 3.0 ml of piperidine, 1.8 ml of acetic acid, 250 ml of benzene, and 61 ml of diethyl malonate was heated overnight at reflux under a Dean-Stark trap,[43] during which time 6.5 ml of water was collected (theory 5.7 ml). The cooled mixture was washed successively with water, dilute hydrochloric acid, water, sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. The filtered solution was fractionated and 92.6 g (90.5%) of **diethyl *o*-2-methylthioethylbenzalmalonate**, n^{24}_D 1.5429, was collected at 159° (0.29 mm) to 163° (0.30 mm).

Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.32; H, 6.09. Found: C, 62.97; H, 6.03.

A mixture of 50.0 g (0.155 mole) of the above malonate and 28.9 g (0.161 mole) of methyl *p*-toluenesulfonate was allowed to stand in a stoppered flask at room temperature for 2 weeks. The solid mass was broken up under dry ether, filtered, washed, and dried *in vacuo* over phosphorus pentoxide. A sample of the crude, white product XIV (67.0 g, 85.1%) was recrystallized from ethanol-ether, mp 77.5-79°.

Anal. Calcd for $C_{25}H_{32}O_7S_2$: C, 59.03; H, 6.34; S, 12.61. Found: C, 58.88; H, 6.77; S, 12.77.

Preparation of Dimethylphenethylsulfonium *p*-Toluenesulfonate.—A mixture of 18.7 g (0.123 mole) of methyl phenethyl sulfide[42] and 22.9 g (0.123 mole) of methyl *p*-toluenesulfonate became turbid after 2 hr. After 3 days the crystalline mass was broken up under ether and filtered. The filtrate, after removal of the ether and further standing at room temperature, deposited further crops of product, total 30.5 g (73.6%). A sample was recrystallized from ethanol, mp 184-184.5°.

Anal. Calcd for $C_{17}H_{22}O_3S_2$: C, 60.33; H, 6.55; S, 18.96. Found: C, 60.17; H, 6.74; S, 19.10.

Electrolysis of XIV.—The catholyte contained 30.6 g (0.06 mole) of XIV, 20.0 g of recrystallized tetraethylammonium *p*-toluenesulfonate, and 130 ml of redistilled dimethylformamide. The anolyte was a solution of the ammonium salt in dimethylformamide. Electrolysis was carried out at 20-25°, 0.50-1.00 amp, and a cathode voltage (sce) of −1.32 v which gradually changed to −2.21 v in the course of 210 min (total amp-hr 3.36). The catholyte, after separation of the mercury, was diluted with ice water and extracted with four 100-ml portions of ether. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. The filtered solution was heated on a water bath to remove ether and dimethyl sulfide (identified as trimethylsulfonium iodide). The residue was vacuum distilled to yield 2.1 g of product, n^{23}_D 1.5041, bp 115° (0.25 mm) to 121° (0.30 mm); there was a red, syrupy residue. Examination of the 2.1 g of distillate by vpc showed that it contained 77.3% of XVII. The identity was checked by the peak-enhancement method. The authentic sample of XVII boiled at 131-133° (0.50 mm), n^{23}_D 1.5031.

Acknowledgment.—We are indebted to the members of the Physical Science Center for performing the various analyses, in particular, D. J. Bauer and R. A. Anderson for nmr interpretation and M. T. Jackson for mass spectrograph interpretation. Thanks are also expressed to Hanne Albertson for obtaining various polarograms.

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(40) E. Schmitz, *Ber.*, **91**, 1133 (1958).

(41) C. F. H. Allen and C. O. Edens, Jr., "Organic Syntheses," Coll. Vol III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 731.

(42) *Cf.* W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).

(43) *Cf.* C. F. H. Allen and F. W. Spangler, ref 41, p 377.

Electrolytic Reductive Coupling. XIV.[1] Concerning the Mechanism of the Intramolecular Electrolytic Reductive Coupling of Bisactivated Olefins at a Mercury Cathode

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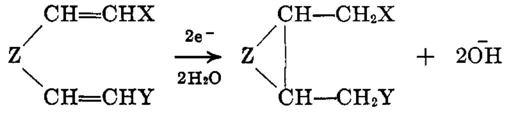
A polarographic study of the esters, $C_2H_5OCOCH{=}CH(\overset{|}{\underset{|}{C}})_nCH{=}CHCO_2C_2H_5$, showed that those members of this series (n = 1-5) which formed cyclic compounds on macroelectrolysis characteristically reduced more easily than model monoolefins, $C_2H_5OCO(CH_2)_5CH{=}CHCO_2C_2H_5$ or ethyl crotonate, while those that did not cyclize reduced at about the same potential as the models. On the basis of the polarographic, microcoulometric, and controlled potential macroelectrolysis, a concerned reduction-cyclization mechanism is proposed for the electrolysis of the bisactivated olefins. The implications of these results for the mechanism of the electrolytic reductive coupling of monoolefins are discussed.

The scope and limitations of intramolecular electrolytic reductive coupling ("electrohydrocyclization," EHC) of bisactivated olefins as a novel synthetic route to cyclic compounds has been discussed.[1]

This paper reports a study of the mechanism of EHC employing polarography, microcoulometry, esr spectroscopy, and macroelectrolysis. In the course of this work an apparently new polarographic phenomenon, the positive shift of cathode potential associated with a concerted reduction/carbon-carbon bond formation,



X and Y are electron-attractive groups, Z is (-C-)$_n$ or a heteroatom

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[1] Paper XIII: J. D. Anderson, M. M. Baizer, and J. P. Petrovich, *J. Org. Chem.*, **31**, 3890 (1966).

was discovered. In addition, the results have a bearing on intermolecular reductive coupling of activated olefins, particularly self-coupling ("electrohydrodimerization," EHD).[2]

A study of the mechanism of EHC provides a particularly favorable starting point for the investigation of the mechanism of electrolytic reductive coupling in general because in EHC the products obtained should be essentially independent of the concentration of the starting material, and the interpretation of the polarographic results may be safely extrapolated to the macroscale. In EHD, on the other hand, the products obtained, hydro dimer or simple reduced monomer, depend importantly on the concentration of the starting material.

Three proposals concerning the mechanism of EHD of activated olefins have been made (eq 1–3). (Analogous formulations, using a bisactivated olefin in place of I, can be made for EHC.) However, each one of these has one or more elements of vulnerability which have consequently demanded ancillary rationalizations.

$$\underset{\text{I}}{\mathrm{RCH{=}CHX}} \xrightarrow{2e^-} \underset{\text{II}}{\mathrm{R\bar{C}H{-}C\bar{H}{\cdots}X}} \xrightarrow[\text{2. 2H}_2\text{O}]{\text{1. RCH=CHX}} \underset{\text{III}}{\mathrm{XCH_2(RCH)_2CH_2X}} + 2\mathrm{OH}^- \quad (1)$$

$$\mathrm{I} \xrightarrow{e^-} \underset{\text{IV}}{\mathrm{RCH{-}\overset{\bar{\cdot\cdot}}{C}H{-}X}} \xrightarrow{\text{RCH=CHX}} \underset{\text{V}}{\mathrm{X{\cdots}\bar{C}H{-}(RCH)_2{-}CH{\cdots}X}} \xrightarrow[\text{2H}_2\text{O, fast}]{e^-} \mathrm{III} + 2\mathrm{OH}^- \quad (2)$$

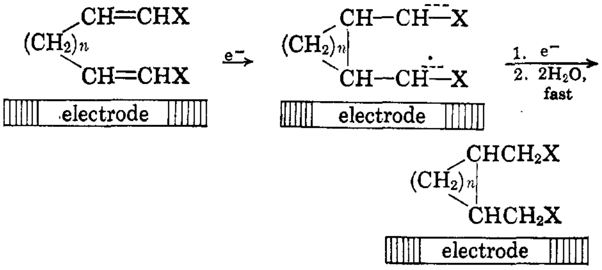
$$1 + \mathrm{H_2O} \xrightarrow{e^-} \underset{\text{VI}}{\mathrm{R\dot{C}H{-}CH_2{-}X}} + \mathrm{OH}^- \xrightarrow[\text{fast}]{e^-} \mathrm{R\bar{C}H{-}CH_2{-}X} \xrightarrow[\text{2. H}_2\text{O}]{\text{1. RCH=CHX}} \mathrm{III} + 2\mathrm{OH}^- \quad (3)$$

The original working hypothesis[2,3] (eq 1) involves the formation of a dianionic intermediate II by a two-electron reduction of I. This proposal has received support from some polarographic studies of acrylonitrile in anhydrous DMF,[1,4] has conveniently explained all the products observed in macroelectrolysis and has led to predictions concerning the scope of electrolytic reductive[2] coupling. However, the apparent two-electron reduction of acrylonitrile in anhydrous DMF may be due to the presence of trace amounts of water in the solvents used which results in the formation of propionitrile as the polarographic product. Furthermore, the addition of two electrons to the monomer at the same potential is energetically improbable.[5] That the coupling step itself is indeed anionic in nature can be seen from the correlation of the yield of dimeric product with the Michael acceptor ability of the olefin, *e.g.*, $\mathrm{CH_2{=}CHCN > CH_2{=}CHCOOC_2H_5 \gg C_6H_5{-}CH{=}CHCOOC_2H_5}$ for EHD.[6-8]

A second plausible mechanism[9] (eq 2) involves a one-electron reduction of the monomer to an anion-radical intermediate IV, which could attack the monomer. The resulting anion radical V could be reduced and protonated yielding hydro dimer III. If either the monomeric IV or dimeric V anion radicals has a significant lifetime, radical-initiated polymeric products would be expected. Under the conditions of the EHD reaction, *i.e.*, in aqueous solutions, no polymeric products are observed.[2]

The electrolytic reduction of acrylonitrile involving water in the initial step (eq 3) leading to the β-cyanoethyl radical VI, as the first intermediate, has been proposed by Beck[10] on the basis of his analysis of Tafel curves. The quantity determined from the Tafel equation is α_n, where α is the transfer coefficient and n is the number of electrons. The assumption that α is 0.5 for organic systems is not necessarily valid.[11] Further, the formation of a β-cyanoethyl radical in preference to the more stable α radical seems very unlikely. There is considerable evidence that a β-cyanoethyl radical, formed in the vicinity of the Hg surface, would react with the electrode, yielding biscyanoethyl mercury, rather than be reduced to the anion at this potential.[12] In the reduction of both triphenylcyanoethylphosphonium bromide[8] and β-iodopropionitrile[13] at a Hg cathode, where the β-cyanoethyl radical is undoubtedly the intermediate, biscyanoethyl mercury was found to be a major product.

Our interpretation of our experimental evidence leads to the proposal (eq 4) that EHC involves a concerted reduction–cyclization during the transfer of the first electron in the potential-determining step followed by rapid hydration and further one-electron reduction. It is postulated that the intermediate anion radical is oriented with the unpaired electron at the electrode surface.



(4)

Results and Discussion

The polarograms of a series of bisactivated olefins, Tables I and II, were obtained in dimethylformamide

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[2] M. M. Baizer, *Tetrahedron Letters*, 973 (1963).

[3] Paper IV: M. M. Baizer, *J. Org. Chem.*, **29**, 1670 (1964).

[4] M. Murphy, M. G. Carangelo, M. B. Ginaine, and M. C. Markham, *J. Polymer Sci.*, **54**, 107 (1961); I. G. Sevast'yanova and A. P. Tomilov, *Zh. Obshch. Khim.*, **33**, 2815 (1963); see in contrast A. V. Finkel'shtein and V. I. Klyaer, *Tr. Sibirsk Teknol. Inst.*, **No. 36**, 106 (1963).

[5] It has been reported that LACO–MO calculations indicate that the reduction of an activated olefin directly to a dianion is possible. No details of the calculation were given. S. Lazarov, A. Trifonov, and T. Vitanov, *Z. Physik. Chem.* (Leipzig), **226**, 221 (1964).

[6] Paper II: M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 223 (1964).

[7] This correlation is, however, not observed in the electrolytic reduction potential of the same monomers, $\mathrm{C_6H_5CH{=}CHCO_2C_2H_5 > CH_2{=}CHCO_2C_2H_5 > CH_2{=}CH{-}CN}$. For a further discussion of this point, see ref 8.

[8] Paper XII: J. H. Wagenknecht and M. M. Baizer *J. Org. Chem.*, **31**, 3885 (1966).

[9] (a) Footnote 18 in paper I.[9b] (b) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

[10] F. Beck, *Chem. Ing. Techn.*, **37**, 607 (1965).

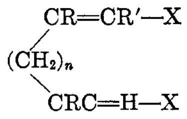
[11] C. L. Perrin, "Progress in Physical Organic Chemistry." Vol. 3, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 171.

[12] J. H. Wagenknecht, unpublished results.

[13] L. G. Feoktistov and S. I. Zhdanov, *Izv. Akad. Nauk SSSR*, **12**, 2127 (1962).

TABLE I

POLAROGRAPHIC REDUCTION OF BISACTIVATED OLEFINS

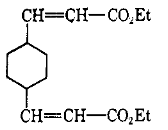
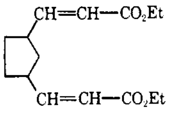
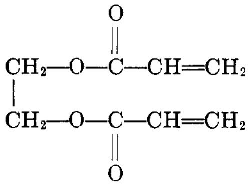
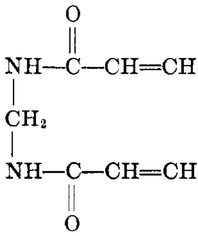


Compd	n	Isomer	R	R′	X	$E_{1/2}$[a]	(I_{d_1}/I_{d_2})[b]	I_{di},[c] %	ΔV[d]	Yield[e] of cyclic compd
VIII[f]	1	...	H	H	CO_2Et	−1.61	1.72	92	0.22	*Ca.* 98
						−1.93	0.15	8		
IX	2	...	H	H	CO_2Et	−1.69	0.84	66	0.14	41
						−1.86	0.43	34		
X	2	...	H	H	$CON(Et)_2$	−1.97	1.03	56	...	...
						−2.12	0.83	44		
XI	2	...	H	H	CN	−1.68	1.45	..	0.17	*g*
XII	2	...	CH_3	H	CO_2Et	−1.82	1.33	64	...	...
						−1.99	0.76	36		
XIII	3	*trans*– *trans*	H	H	CO_2Et	−1.65 −1.97	1.35 0.24	85 15	0.18	*Ca.* 100
XIV	3	*cis*– *trans*	H	H	CO_2Et	−1.65 −1.97	1.57 0.27	85 15	0.18	...
XV	3	...	H	C_6H_5	CO_2Et	−1.59	1.19	84	...	65
						−1.93	0.23	16		
XVI	4	*trans*– *trans*	H	H	CO_2Et	−1.68 −1.87	1.17 0.42	74 26	0.15	81
XVII	4	*cis*– *trans*	H	H	CO_2Et	−1.68 −1.87	1.19 0.36	77 23	0.15	...
XVIII	5	...	H	H	CO_2Et	−1.79	2.03	..	0.04	10
XIX	6	...	H	H	CO_2Et	−1.83	1.85	..	...	0
XX	12	...	H	H	CO_2Et	−1.83	1.90	..	...	0

[a] $E_{1/2}$ *vs.* Hg pool with 0.2 M $Bu_4N^+Br^-$. [b] Concentration of olefin 1.8–2.1 × 10^{-3} M. [c] 100 × $(I_{d_1}/I_{d_1} + I_{d_2})$ and 100 × $[I_{d_2}/(I_d + I_{d_2})]$ using ethyl crotonate and crotononitrile as models. [e] Reference 1. [f] Aliphatic hydrogens were replaced by ethyl radicals. [g] Polymerizes on electrolysis; see Discussion.

TABLE II

POLAROGRAPHIC REDUCTION OF MISCELLANEOUS BISACTIVATED OLEFINS

Compd	10^3M	$E_{1/2}$[a]	I_d
 XXI	0.96	−1.81	1.67
 XXII	2.03	−1.73 −1.92	1.04 0.50
 $\mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2}$ $\mathrm{CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2}$ XXIII	1.43	−1.57	1.28
 $\mathrm{NH{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2}$ $\mathrm{CH_2}$ $\mathrm{NH{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2}$ XXIV	0.67	−1.77 −2.17	1.09 1.43

[a] $E_{1/2}$ *vs.* Hg pool with 0.2 M $Bu_4N^+Br^-$.

(DMF) solution containing 0.2 M tetra-*n*-butylammonium bromide.[14] The bisactivated olefins which yielded ring compounds on large-scale electrolysis[1] were found to reduce polarographically at a voltage which was to a small but reproducible extent displaced anodically from the half-wave potentials determined for model simple activated olefins of similar structure (Table III). This positive shift *usually* resulted in the development of *two* reduction waves (Figure 1) discernible with more (Figure 1a) or less (Figure 1b) difficulty. The more anodic wave was associated with the cyclization reaction, the more negative wave with linear reactions. Since the ratio of wave heights and the magnitude of the $E_{1/2}$ shifts correlate with the extent of cyclization (*vide infra*), the two waves are most differentiated when cyclization is *ca.* 40–70% of the total reaction but tend to merge into one wave when cyclization constitutes a very high (XI) or a very low (XVIII) portion of the total reaction. It should be noted that even when

TABLE III

POLAROGRAPHIC REDUCTION OF MODEL OLEFINS

Compd	10^3M	$E_{1/2}$[a]	I_d
Ethyl crotonate	1.68	−1.82	1.15
Crotononitrile	1.58	−1.85	1.60
Diethyl 2-nonene-1,9-dioate	2.15	−1.84	1.04

[a] $E_{1/2}$ *vs.* Hg pool with 0.2 M $Bu_4N^+Br^-$.

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[14] This system gave the most satisfactory results. Severe maxima problems were encountered with both aqueous acetonitrile and ethanol as solvents.

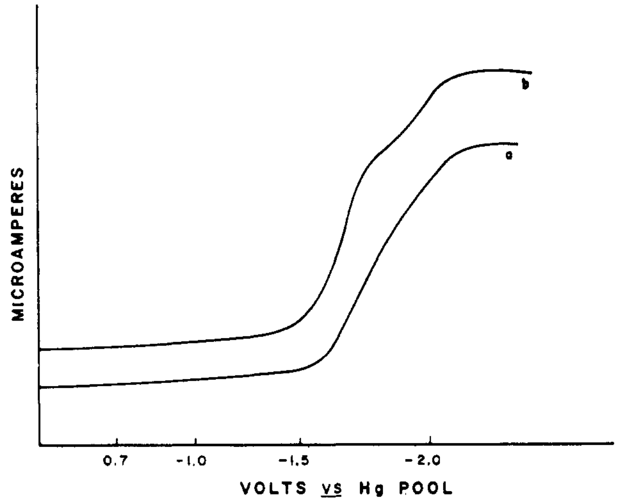


Figure 1.—Polarographs of (a) diethyl 2,6-octadiene-1,8-dioate, (b) diethyl 2,7-nonadiene-1,9-dioate with DMF as solvent.

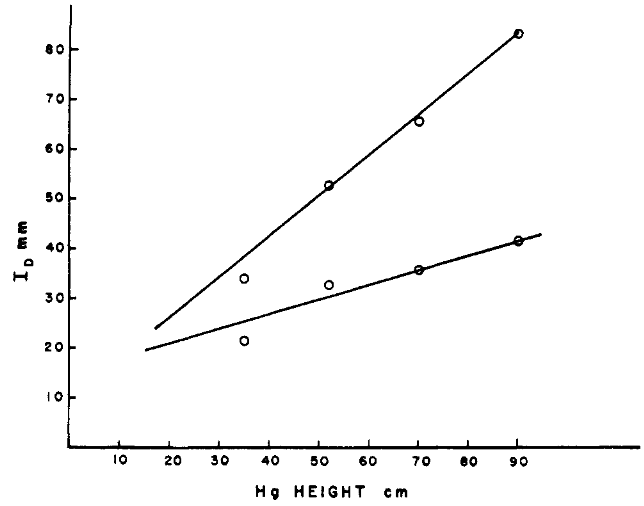
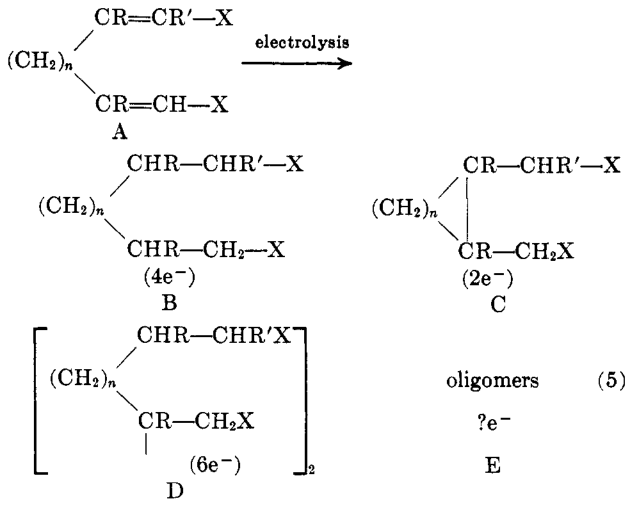


Figure 2.—Plot of I_d vs. H for diethyl 2,6-octadiene-1,8-dioate.

only one polarographic wave is obtained, *if the* $E_{1/2}$ *is positive with respect to that of a reference compound, cyclization has occurred.*

The total I_d values obtained from the polarogram show marked deviations from compound to compound, Table I, column 8. The values were reproducible for a given compound. This apparent anomaly can be explained on the basis of the possible products of the reduction (eq 5). The macroelectrolysis of bisactivated olefins, A, has been shown to be capable of yielding saturated monomer B ($4e^-$), cyclic compounds C ($2e^-$), saturated hydro dimer D ($3e^-$), and higher boiling compounds E ($?e^-$) in varying amounts depending on the structure of the starting material and on the electrolysis conditions.



(5)

The actual number of electrons involved in these reductions was determined coulometrically for selected compounds, Table IV. For diolefin XIII, which yielded cyclic product quantitatively in macroelectrolysis, the electron uptake per molecule was 1.98 in aqueous acetonitrile solution and initially 2.01 in anhydrous DMF. The downward drift in the electron uptake observed in this case is probably due to the reaction of the cyclic anionic product with unreacted olefin forming dimeric and possibly oligomeric products. In the other cases, where little (XVIII) or no (XIX) ring compound was obtained, the number of electrons per molecule was considerably higher.

TABLE IV

COULOMETRY OF SOME BISACTIVATED OLEFINS

Compd	Solvent	10^3M	n^a
XIII	Anhydrous DMF	1.97	2.01, 1.24[b]
XIII	Aqueous CH_3CN, 80%	2.38	1.98
XVIII	Aqueous CH_3CN, 80%	1.63	3.29
XIX	Aqueous CH_3CN, 80%	1.66	3.34

[a] $n = i_0/CVFk$, where k is the slope of the line from a plot of ln i vs. time. [b] Plot curved, initial and final slopes taken.

It has been reported that the first wave of a two-wave polarogram may in some cases be explained on the basis of the adsorption of the depolarizer on the electrode surface.[15] When this has been the case, the wave height, I_d, has been a linear function of the height of the Hg column. Polarograms of diolefin IX were determined as a function of the Hg reservoir height, H. The data are given in Table V. A plot of I_d vs. H (Figure 2) is not linear. In contrast, the plot of I_d vs. $\sqrt{H}$ (Figure 3) is more nearly linear. These observations are consistent with a diffusion-controlled process rather than with an adsorption phenomenon. In addition, if the first wave were due to adsorption, one would expect to find similar adsorption of other compounds with the same functionality. This, however, is not observed, *e.g.*, diolefins XIX and XX.

TABLE V

POLAROGRAPHIC REDUCTION OF DIETHYL 2,6-OCTADIENE-1,8-DIOATE IN DMF WITH 0.2 M TETRABUTYLAMMONIUM BROMIDE AT VARIOUS MERCURY RESERVOIR HEIGHTS

Hg height, cm	I_{d_1}, mm	I_{d_2}, mm
90	84	42
70	66	36
52	53	33
35	34	23

By comparing the fractional height of the first wave, $I_{d_1}/(I_{d_1} + I_{d_2}$ (Table I, column 8) with the yield of cyclic derivative resulting from macroelectrolysis (Table I, column 10) a nearly linear relationship is found. The fractional height of the first wave as well

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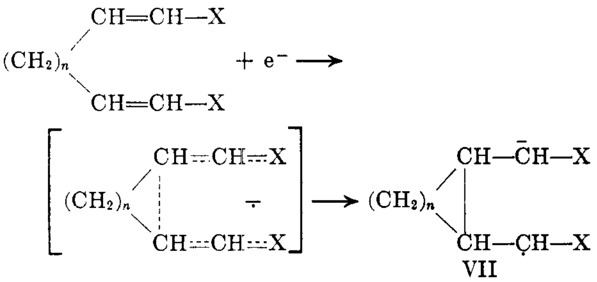
(15) R. Brdicka, *Collection Czech. Chem. Commun.*, **12**, 522 (1947).

as the positive shift in $E_{1/2}$ are proportional to the yield of cyclic compounds. One exception was observed, diolefin XV. The only observed product in this case was the cyclic derivative. Since only about 70% of the starting material was accounted for in the work-up, the reported yield is undoubtedly low.

On the basis of the polarographic data, it is clear that both double bonds are involved in the electrolytic reduction at the more positive potential. The effect is not transmitted through the aliphatic chain, since the effect where $n = 3$ (diolefin XIII) is greater than when $n = 2$ (diolefin IX). The positive shift in $E_{1/2}$ parallels the ease of ring formation and is most reasonably ascribed to partial carbon–carbon bond formation. On this basis, therefore, the transition state for the electrolytic reduction involves *both* double bonds, as shown in eq 6. In this depiction both activating groups



(6)

VII

stabilize the transition state is a greater or lesser extent depending on the degree of bond formation which in turn depends upon the ease of ring formation.

A study of the molecular models of diolefins VIII and XIII shows that the double bonds can be parallel and the carbon atoms β to the carbethoxy groups can be brought to within about one carbon–carbon bond distance apart without serious steric interactions. With diolefins IX and XVI, a parallel alignment of the double bonds is difficult and there is some steric hindrance in attempting to bring the β-carbon atoms within one bond length apart. The steric interactions are even more severe for diolefin XVIII.

The mechanism of the EHC reaction, therefore, most probably involves a concerted one-electron reduction of both double bonds forming the cyclic anion radical VII on the Hg surface. This anion radical is then rapidly reduced to the corresponding dianion. The protonation of the dianion by water yields the observed products. In contrast to a β-X-ethyl radical, which would be expected to form Hg compound,[8,13] the α radical VII would be expected to be reduced to the anion. The electrolytic reduction of triphenylcyanomethyl phosphonium bromide involves two electrons yielding directly the α anion.[8] This reduction occurs at a more positive potential than that of the corresponding cyanoethyl derivative under the same conditions.

In the reduction of bisactivated olefins the major competing reaction to EHC is simple linear reduction. Polarographically this is manifested at the same voltage as is the reduction of model olefins (Table III). This reduction leads largely to saturated monomer under polarographic conditions and hydro dimer in macroelectrolysis.

The mechanism as proposed (eq 6) predicts that the product of electrolytic reduction of the bisactivated olefins can be controlled by controlling the working-electrode potential. A macroelectrolysis conducted at the more positive potential should form more cyclic compound than a similar electrolysis conducted at a higher potential.

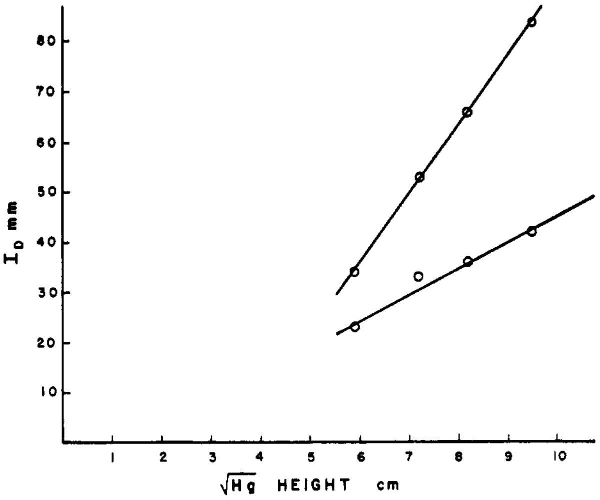


Figure 3.—Plot of I_d *vs.* $\sqrt{H}$ for diethyl 2,6-octadiene-1,8-dioate.

The data for the controlled-potential electrolysis of bisactivated olefin IX are given in Table VI. With the potential controlled externally at −1.95 v *vs.* sce, the yield of cyclic derivative was 38%. As the potential was increased, the yield of cyclic derivatives decreased as predicted by the proposed mechanism.

TABLE VI

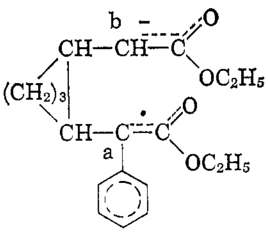
CONTROLLED POTENTIAL ELECTROLYSIS OF DIETHYL 2,6-OCTADIENE-1,8-DIOATE

Run	Monomer,[a] g	Potential, v[b]	Current, amp	Yield of cyclic compd,[c] %
1	25	−1.95	0.6–0.1	38.3
2	25	−2.05	0.75–0.2	17.1
3	25	−2.0–2.5	2.0	1.7

[a] With 80 ml of CH_3CN, 30 g of $Et_4N^+OTS^-$, 15 ml of H_2O. [b] *Vs.* sce. [c] Based on current input.

There are three interrelated means of changing the potential of a given working electrode. With the same electrode surface area, changing the concentration of depolarizer, altering current density, and finally controlling the voltage externally can produce similar effects. The macroelectrolysis yield for olefin IX given in Table I was obtained with a twofold increase in concentration of depolarizer. This increased concentration of depolarizer effectively kept the potential of the working electrode below −1.95 v *vs.* sce at 2 amp for a good portion of the electrolysis. Therefore, most or all of the cyclic product observed was found in the early stages of the macroelectrolysis.

It is interesting to note that, during the macroelectrolysis of the unsymmetrically substituted diolefin XV, a red color was observed at the electrode surface.[1] Since this diolefin showed a two-wave polarogram (−1.59 and −1.93 v), the cyclic derivative is being formed by a concerted reduction–cyclization. The α-phenyl-substituted activated olefinic site a reduces at a more positive potential than the other activated olefinic site b; therefore, the first reduction must occur with a oriented at the electrode surface. The immediate result of the electron transfer to the molecule in this orientation is the formation of a substituted benzyl radical and an α-carbethoxy anion. The red color is undoubtedly due to this benzyl radical.[16] Attempts to observe this radical by epr spectroscopy are underway.



The fact that this phenyl-substituted diolefin (XV) does form cyclic derivative, when only one of the olefins can reduce at this potential (1.60 *vs.* Hg pool) rules out any mechanism involving the independent reduction of both double bonds followed by either a dimerization of anion radicals or a protonation and dimerization of simple radicals to form the observed ring compounds. This fact points out a significant difference between the EHC reactions and the acyloin reaction, which involves the reduction of both ester groups by sodium and the subsequent ring closure by radical dimerization.[17]

In the electrolytic reduction of bisactivated olefins, there is a considerable driving force for cyclization. Using diolefin XIX as a model for the expected $E_{1/2}$ for the simple reduction of the double bonds, an energy difference (Table I, column 10) of between 5 kcal for diolefin VIII and 0.92 kcal for diolefin XVIII can be calculated.[18] Analogous driving forces favoring ring formation have been observed in other chemical systems. The ultraviolet spectrum of bicycloheptadiene[19] has been shown to involve interaction between the parallel double bonds in the excited state. The bromination of bicycloheptadiene yields a dibromo compound with the nortricyclene structure. Bartlett and Bank[20] have observed that the rate of acetolysis of β-(cyclopenten-3-yl)ethyl *p*-nitrobenzenesulfonate is 95 times the acetolysis rate of the saturated analog and that the product is the cyclic derivative, *exo*-norbornyl acetate. Butler and Raymond[21] have pointed out that cyclic polymerization of diolefins is a highly favored reaction. Probability calculations predict only 50% ring formation in the polymerization of 1,6-heptadiene. However, experimental results show 95–100% cyclic polymerization in the concentration range of 1.9–8.0 *M*.

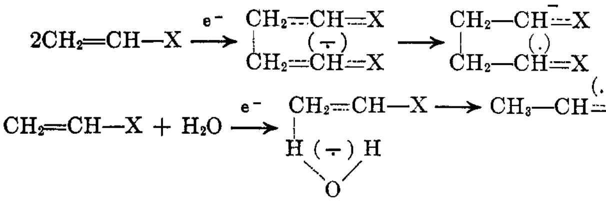
The effect of activating group X (Table I) parallels a similar effect in the EHD reaction. Using per cent I_d for the first wave as an indication of the extent of formation of cyclic products, the order for the activating groups for EHC is CN >> $CO_2C_2H_5$ > $CO_2N(C_2H_5)_2$, 100, 66, 56, respectively. With diolefin XI, where X = CN, only one polarographic wave was observed and $E_{1/2}$ was shifted 0.17 v from the expected value of −1.85 v for crotononitrile (Table II). The existence of only one polarographic wave, positive with respect to crotonitrile, predicts, on the basis of the proposed mechanism, exclusive formation of ring compound on macroelectrolysis. The cyano group greatly favors ring formation. This prediction has neither been confirmed nor negated by experiment. Macroelectrolysis of XI under normal conditions, pH 7–9, gave only oligomeric products probably arising from chemical initiation. Another experiment, under acidic conditions, pH 5–6, yielded only the cyclobutane compound as the electrolysis product. However, since a poor material balance was obtained it appears as though the competing side reactions are too fast in this case to allow any unambiguous conclusions to be drawn from these results.[22]

A β-methyl substituent (diolefin XII) shifts the reduction potential in the negative direction, as is expected,[23] but has virtually no effect on the relative heights of the two polarographic waves.

The effect of geometric isomers on the EHC reaction has also been studied. With diolefins XIII, XIV, XVI, and XVII, it can be seen that there is virtually no difference in the reduction potential nor the relative wave heights on changing from pure *trans–trans* to *cis–trans* isomers. This is in contrast to the reduction of monoolefinic esters where the *cis* isomer usually reduces at a more positive potential than the *trans*.[24]

The EHC reaction was extended to the formation of bicyclic derivatives. With diolefin XXII, two waves were observed polarographically and the cyclic derivative was found on macroelectrolysis. Only one unshifted wave was observed with diolefin XXI, indicating little or no cyclization. This is not unreasonable since in the case of XXI the cyclization would have to occur through the highly unfavorable boat conformation.

It is very tempting at this time to apply this concerted reduction mechanism of bisactivated olefins to simple monoolefins. It has several advantages over other mechanistic proposals (eq 1–3). The most glaring inconsistency in any reduction mechanism involving only one molecule of monomer is that the intermediate, presumably anionic in character, must be neutralized almost exclusively in the first step by monomer and the resulting dimeric anion must be neutralized exclusively by water.[25] In contrast, the concerted mechanism requires that the reduction potential of the monomer-assisted reduction of the monomer to form dimer take place at a slightly more positive potential than the water-assisted reduction to form saturated



$$2\mathrm{CH_2{=}CH{-}X} \xrightarrow{e^-} \begin{array}{l} \mathrm{CH_2{\cdots}CH{\cdots}X} \\ \mid \qquad (\dot{-}) \\ \mathrm{CH_2{\cdots}CH{\cdots}X} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_2{-}\overset{-}{CH}{\cdots}X} \\ \mid \qquad (.) \\ \mathrm{CH_2{-}CH{\cdots}X} \end{array} \tag{7}$$

$$\mathrm{CH_2{=}CH{-}X + H_2O} \xrightarrow{e^-} \begin{array}{l} \mathrm{CH_2{\cdots}CH{-}X} \\ \mid \\ \mathrm{H\ (\dot{-})\ H} \\ \quad \diagdown \ \diagup \\ \qquad \mathrm{O} \end{array} \longrightarrow \mathrm{CH_3{-}\overset{(.)}{CH}{\cdots}X}$$

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[16] The benzyl anion formed from diethyl phenylmalonate and sodium hydride in DMF is yellow in color.

[17] S. M. McElvain, *Org. Reactions*, **4**, 256 (1948).

[18] These estimates are undoubtedly high since the contribution from the irreversibility of the reaction is not considered here.

[19] S. Winstein, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[20] P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

[21] G. B. Butler and M. A. Raymond, *J. Polymer Sci.*, **3**, 3413 (1965).

[22] Reference 1, especially footnotes *c* and *d* of Table II.

[23] M. M. Bargain and M. M. Delepine, *Compt. Rend.*, **255**, 1948 (1962).

[24] A. L. Markmann and E. V. Zinkova, *Zh. Obshch. Khim.*, **27**, 1438 (1957).

[25] As a possible explanation of this phenomenon, it has been proposed that, in the presence of a tetraalkylammonium salt, little or no water is in the vicinity of the electrode; see L. G. Feoktistov, A. P. Tomilov, and I. G. Sevast'yanova, *Electrokhimiya*, **1**, 1300 (1965).

monomer. In each case, the radical product would be formed at the electrode surface and therefore would be expected to reduce to the anion. The anions would all be neutralized by water. (In anhydrous systems polymerization would occur.) With these points in mind, the mechanism of the EHD reaction is under investigation.

Experimental Section

Apparatus.—All polarograms were obtained with a Sargent Model XXI polarograph. The dropping mercury electrode constants were $m^{2/3} = 1.45$, $t^{1/6} = 1.33$. Heyrovsky cells were used throughout this work and the polarograms were recorded against a Hg pool with 0.2 *M* tetrabutylammonium bromide in anhydrous dimethylformamide solution. Cell resistances were between 300 and 600 ohms.

The microcoulometry was done with a Beckman Electroscan 30 using a Hg pool as the cathode and silver–silver iodide as the anode and a sce as the reference. The salt bridges used were glass frits with a saturated solution of tetraethylammonium bromide in appropriate solvents.

Materials.—Diethyl 3,3-diethyl-2,5-heptadiene-1,7-dioate (VIII), diethyl 2,6-octadiene-1,8-dioate (IX), diethyl 2,7-nonadiene-1,9-dioate (XIII and XIV), diethyl 2,8-decadiene-1,10-dioate (XVI and XVII), diethyl 2,9-undecadiene-1,11-dioate (XVIII), diethyl 2,10-dodecadiene-1,12-dioate (XIX), diethyl 2,16-octadecadiene-1,18-dioate (XX), and diethyl 2-phenyl-2,7-nonadiene-1,9-dioate (XV) were samples of these compounds prepared by J. D. Anderson.[1] 1,6-Dicyano-hexa-1,5-diene (XI) was obtained from Monsanto Research Corp., Dayton, Ohio. Ethylenebisacrylate (XXIII) was obtained from Borden Chemical Co. N,N′-Methylenebisacrylamide (XXIV) was obtained from Chemicals Procurement Laboratories, Inc.

Synthesis of Diethyl 3,6-Dimethyl-2,6-octadiene-1,8-dioate (XII).—To a slurry of NaH (4.3 g of 55% dispersion in mineral oil, 0.1 mole) in 200 ml of dimethoxyethane, dried over calcium hydride, was added diethyl phosphonoacetate[26] (22.4 g, 0.1 mole) dropwise at 20°. The resulting solution was stirred until the hydrogen evolution ceased (*ca.* 1 hr). To this yellow solution was added 2,5-hexadione (5.7 g, 0.05 mole) and the resulting mixture was stirred overnight. The resulting mixture, containing a gummy precipitate, was poured into 500 ml of water and extracted two times with 250-ml portions of ether. The ether solution was dried over magnesium sulfate and filtered, and the ether was removed by distillation. Distillation of the brown oil at reduced pressure gave 6.6 g (50%), bp 105–106° (0.1 mm), $n^{27}\mathrm{D}$ 1.4762.

Anal. Calcd for $C_{12}H_{18}O_4$: C, 66.11; H, 8.72. Found: C, 66.37; H, 8.77.

Vpc analysis of this material showed three peaks in about 60:35:5 ratio which correspond to *trans–trans*, *cis–trans*, and *cis–cis* isomers. Assignments were made on the basis of the nmr spectrum of the mixture. Infrared analysis showed the characteristic spectrum of an α,β-unsaturated ester.[2]

Synthesis of Bis(N,N-diethylamide) of 2,6-Octadienedioic Acid (X).—α,α¹-**Dibromosuberoyl chloride**, prepared by the method of Lüttringhause and Merz,[27] was added at ice-bath temperature in a 1:4 mole ratio to diethylamine dissolved in benzene. The amine hydrochloride salt, which precipitated out, was removed by filtration, and the filtrate was washed with water and sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed leaving crude **N,N,N′,N′-tetraethyl-α,α′-dibromosuberamide**. Twenty-five grams of this crude amide (0.06 mole) was refluxed with 75 ml of DMF[28] for 6 hr. The reaction mixture was diluted with water and extracted with methylene chloride, and the solvent was dried and removed. Distillation of the residue gave 6 g (33%) of (X), bp 178° (0.15 mm), $n^{25}\mathrm{D}$ 1.5223.

Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.57; H, 10.00; N, 10.00. Found: C, 68.90; H, 9.13; N, 9.46.

Synthesis of *cis*-Diethyl 1,4-Cyclohexanediacrylate (XXI).—*cis*-1,4-Bis(hydroxymethyl)cyclohexane (200 g, 1.4 moles) was added dropwise at 15–20° to a solution of phosphorus tribromide (376.3 g, 1.4 moles) in 300 ml of benzene. The mixture was stirred at room temperature for 6 hr and then heated to reflux for 8 hr. The reaction mixture was then poured into ice water and extracted with methylene chloride. The extracts were washed with sodium carbonate solution and dried over magnesium sulfate. Distillation of the residue after removal of solvent gave *cis*-**1,4-bis(bromomethyl)cyclohexane** (193.6 g, 52%), bp 135° (8 mm), $n^{25}\mathrm{D}$ 1.5362.

Anal. Calcd for $C_8H_{14}Br_2$: C, 35.56; H, 5.19; Br, 59.25. Found: C, 35.45; H, 5.27; N, 59.48.

Diethyl malonate (256 g, 1.6 moles) was added dropwise at 0–5° to a slurry of 55% sodium hydride–mineral oil (67 g, 1.55 moles) in 600 ml of DMF. When the hydrogen evolution had ceased, *cis*-1,4-bis(bromomethyl)cyclohexane (191.6 g, 0.71 mole) was added dropwise. An exothermic reaction took place, The reaction mixture was then warmed on a steam bath for 5 hr. Dilution of the reaction mixture with water, followed by extraction with methylene chloride, drying, removal of solvent, and distillation of the residue gave 168.8 g (55%) of *cis*-1,4-bis-(β,β-diethoxycarbonylethyl)cyclohexane, bp 217° (0.95 mm), $n^{25}\mathrm{D}$ 1.4590.

Anal. Calcd for $C_{22}H_{36}O_8$: C, 61.68; H, 8.41. Found: C, 61.50; H, 8.66.

The above intermediate (99.8 g, 0.23 mole), 180 ml of 6 *N* hydrochloric acid, and 80 ml of glacial acetic acid were heated at reflux for *ca.* 20 hr. The "volatiles" were removed under vacuum; the residue was heated to 170–180° with a mineral oil bath to decarboxylate the material. The resulting crude product was recrystallized from water giving 44.4 g (85% yield based on the tetraester) of *cis*-**1,4-cyclohexanedipropionic acid**, mp 124–125°.

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Found: C, 63.16; H, 8.53.

The dicarboxylic above was converted to *cis*-**diethyl 1,4-cyclohexanediacrylate** using the general procedure of Anderson, *et al.*[1] The product, $n^{25}\mathrm{D}$ 1.4971, was purified using a Kontes semi micro falling film still at 180° (0.02 mm).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.57; H, 8.57. Found: C, 68.72; H, 8.27.

Solvents.—Dimethylformamide was distilled from barium oxide through a 6-ft, glass-helix-packed column. Acetonitrile was purified by rapid distillation of a solution containing 1 ml of concentrated sulfuric acid per liter of acetonitrile followed by distillation from calcium hydride through a 6-ft, glass-helix-packed column.

Separation of the Geometric Isomers of Diethyl 2,7-nonadiene-1,9-dioate and Diethyl 2,8-Decadiene-1,10-dioate.—A mixture of *ca.* 80% diethyl *trans,trans*-2,7-nonadiene-1,9-dioate and 20% diethyl *cis,trans*-2,7-nonadiene-1,9-dioate was separated by preparative vpc on a F & M Model 770 automatic preparative vpc modified with an electrostatic precipitator[29] using a 8-ft × 0.75 in. column packed with 1% $AgNO_3$, 18% Carbowax 20 on Chromosorb W at 210°. Recovery was about 80%. The isomers XIII, $n^{25}\mathrm{D}$ 1.4708, and XIV, $n^{25}\mathrm{D}$ 1.4682, were at least 95% pure by analytical vpc, using a 3 m × 0.25 in. column packed as described above at 180°. The same procedure was used for the separation of diethyl *trans,trans*-2,8-decadiene-1,10-dioate XVI, $n^{25}\mathrm{D}$ 1.4706, and diethyl *cis,trans*-2,8-decadiene-1,10-dioate XVII $n^{25}\mathrm{D}$ 1.4682. The column temperature was 230° and the recovery was 76%. The isomers were at least 95% pure by analytical vpc as described above.

Controlled Potential Electrotypes of Diethyl 2,6-Octadiene-1,8-dioate (IX).—The apparatus and general electrolysis procedure used in these experiments have been described.[9b] An Analytical Instruments Inc. potentiostat was used for controlling the cathode voltage. The catholyte compositions, cathode potentials, currents, and yields of the cyclic product, diethyl 1,2-cyclobutanediacetate,[30] are summarized in Table VI.

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[26] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

[27] A. Lüttringhaus and H. Merz, *Arch. Pharm.*, **293**, 881 (1960).

[28] The use of amides as reagents for dehydrohalogenation has been described: J. D. Anderson, submitted for publication.

[29] W. D. Ross, J. F. Moon, and R. L. Erees, *J. Gas Chromatog.*, **2**, 340 (1964).

[30] Identified by vpc comparison with an authentic sample previously characterized; see ref 1.