developed[32] for the preparation of the corresponding bromide. A mixture of 131 g (0.5 mole) of triphenylphosphine, 95 g (0.5 mole) of *p*-toluenesulfonic acid monohydrate, and 100 ml (excess) of stabilized acrylonitrile was heated for 40 min under reflux. Volatile materials were then removed on the water bath *in vacuo*. The residue was taken up in 300 ml of water and filtered. The filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized from acetone yielding 220 g (90.6%) of product, mp 104–105.5°.

Anal. Calcd for $C_{28}H_{26}NO_3PS$: C, 68.97; H, 5.38; P, 6.15; S, 6.58. Found: C, 68.86; H, 5.40; P, 6.32; S, 6.62.

Preparation of Triphenylcyanopropylphosphonium Bromide (V).—This salt was prepared from triphenylphosphine and 4-bromobutyronitrile in refluxing benzene or ethyl acetate. The product (79.5%) after recrystallization from ethanol melted at 218–219°.

Anal. Calcd for $C_{22}H_{21}BrNP$: C, 64.39; H, 5.13; Br, 19.48. Found: C, 64.32; H, 5.25; Br, 19.60.

Compound VI was prepared similarly from 5-bromovaleronitrile. After several days of reflux, 78.5% of crude product was obtained which, after recrystallization from ethanol, melted at 223–224°.

Anal. Calcd for $C_{23}H_{23}BrNP$: C, 65.09; H, 5.44; Br, 18.83. Found: C, 65.11; H, 5.46; Br, 19.01.

Attempted Structure Proof of XIV *via* Ethyl Styrylacrylate.—Styrylacrylic acid was prepared on the scale reported.[33] The crude product (90.0 g) was esterified with ethanol and *p*-toluenesulfonic acid. The esters were fractionated through a 2-ft Vigreu column yielding (1) 43.1 g, bp 135° (1.2 mm) to 138° (1.3 mm), n^{23}D 1.6148, and (2) 8.9 g, bp 139–145° (1.2 mm), n^{23}D 1.6130, along with higher boiling residue. Vpc examination showed that each fraction contained two isomers (geometric). Fraction 1 was analyzed.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.97. Found: C, 77.09; H, 6.90.

Forty grams (0.198 mole) was hydrodimerized to partial conversion (2.70 amp-hr) according to the general procedure described.[29] The crude product, after removal of 17.9 g of starting material by fractional distillation, was 20.1 g of a syrupy, yellow liquid. Addition of ethanol caused precipitation of 5.7 g of one of the isomers (XIX), mp 130–130.5°, of **diethyl 3,4-bisstyryladipate.**[34] The alcoholic mother liquor (XX) contained other isomers.

Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.89; H, 7.44. Found: C, 76.87; H, 7.45.

XIX (4.9 g) was suspended in 60 ml of ethanol, 0.5 g of 5% palladium on charcoal was added, and the mixture was hydrogenated on a Parr shaker at an initial pressure of 31 psi. The theoretical amount of hydrogen (2.0 psi) was taken up in 30 min. Fractionation of the filtered solution yielded 4.2 g, bp 203° (0.25 mm) to 208° (0.25 mm) (main portion) to 210° (0.30 mm), n^{24}D 1.5190, of **diethyl 3,4-bis-2-phenethyladipate** (XXI). Vpc examination (silicone grease at 250°) showed only one component.[31]

Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35. Found: C, 75.73; H, 7.46.

Hydrolysis of XXI with 1:1 hydrochloric acid–water followed by reprecipitation of the crude diacid product from alkaline solution and recrystallization from dilute ethanol yielded XXII, **3,4-bis-2-phenethyladipic acid,**[30] mp 136–138°.

Anal. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.58; H, 7.62.

Catalytic hydrogenation of XX according to the procedure described above yielded (1) 3.3 g of XXI isomer, bp 201–212° (0.2 mm), n^{23}D 1.5230, and (2) 8.8 g of XXI isomer, bp 212° (0.25 mm) to 214° (0.30 mm), n^{23}D 1.5224. Hydrolysis of product 1 with concentrated hydrochloric acid yielded a diacid, mp 158–159° (from ethanol), which on reesterification produced as ester, XXIII, bp 170° (0.07 mm), n^{24}D 1.5190. The nmr spectrum of this compound consisted of a singlet at τ 2.90 (10 H) for the aromatic hydrogens, a quartet at 5.96 (4 H), and a triplet at 8.81 (6 H) for the ethoxy groups, a triplet at 7.50 (4 H) for the methylenes α to the phenyl groups, a broad singlet at 7.85 (4 H) for the methylenes α to the carbonyl groups, and a multiplet at 8.47 (6 H) for the hydrogens β and γ to the phenyl groups. This spectrum differs from that of XVIII given above.

Acknowledgment.—The authors wish to thank M. T. Jackson, Jr., and D. J. Bauer for obtaining and interpreting some of the spectroscopic data.

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(32) H. Hoffmann, *Chem. Ber.*, **94**, 1331 (1961).

(33) A. G. Anderson and S. Y. Wang, *J. Org. Chem.*, **19**, 277 (1954).

(34) This structure is inferred from the nmr data given below for the saturated ester.

Electrolytic Reductive Coupling. XIII.[1] Intramolecular Reductive Coupling. Electrohydrocyclization[2]

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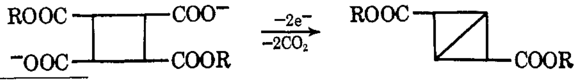
Electrolytic reductive coupling has been extended to intramolecular reactions which have been found capable of yielding a wide variety of cyclic compounds. A series of bisactivated olefins, $ROOCCH{=}CH(CR_2)_nCH{=}CHCOOR$, gave high yields of ring compounds by β-to-β coupling when n was 1, 2, 3, and 4; the proposed mechanism of the reaction explained the fact that only acyclic products were formed when n was greater than 4. The reaction was also useful in the syntheses of bicyclic and heterocyclic compounds. Thus, the electrolysis of *cis*-diethyl 1,3-cyclopentanediacrylate gave *trans*-diethyl 2,3-norbornanediacetate and the electrolysis of 1,2-bis(2-ethoxycarbonylvinyloxy)ethane gave 2,3-bis(ethoxycarbonylmethyl)-1,4-dioxane. A variation of the reaction gave a cyclic product by an electrolytic displacement reaction: dimethyl *o*-[(bis-β-ethoxycarbonyl)vinyl]phenethylsulfonium *p*-toluenesulfonate gave 3-indanylmalonate.

The development of synthetic methods for the preparation of cyclic compounds has engaged the interest of many investigators. The numerous *chemical* methods that have become available have been reviewed.[3] Little has been reported on direct *electrochemical* routes to cyclic compounds. Attempts to prepare cycloalkanes *via* Kolbe reactions with dicarboxylic acids had been unsuccessful[4] until Vellturo and Griffin[5] described the preparation of a bicyclobutane derivative by this procedure.



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

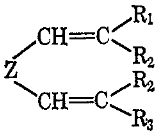
(2) Preliminary communication: J. D. Anderson and M. M. Baizer, *Tetrahedron Letters*, 511 (1966).

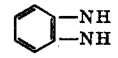
(3) See, for example, (a) E. Vogel, *Angew. Chem.*, **72**, 4 (1960); (b) M. Julia, *Rec. Chem. Progr.*, **25**, 3 (1964); (c) L. I. Belinkii, *Russ. Chem. Rev.*, 551 (1964); (d) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. 2A, Elsevier Publishing Co., New York, N. Y., 1953; (e) K. T. Finley, *J. Chem. Educ.*, **42**, 536 (1965).

(4) G. E. Svadkovskya and S. A. Voitkevich, *Russ. Chem. Rev.*, 161 (1960), and references contained therein.

(5) A. F. Vellturo and G. W. Griffin, *J. Am. Chem. Soc.*, **87**, 3021 (1965).

TABLE I[a]
BISACTIVATED OLEFINS USED IN THE EHC INVESTIGATION



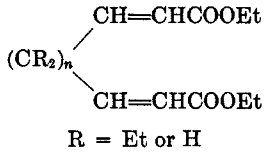
Diolefin[b,c]	Z	R_1	R_2	R_3	Bp, °C (mm)	n^{25}_D	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
I	EtCEt	H	COOEt	H	123 (0.2)	1.4770	$C_{15}H_{24}O_4$	67.16	8.96	66.21	9.05
II	$(CH_2)_2$	H	COOEt	H	102 (0.2)	1.4758	$C_{12}H_{18}O_4$	63.72	7.96	63.46	7.89
III[d]	$(CH_2)_2$	H	CN	H	...	...	...	...	...	...	...
IV	$(CH_2)_3$	H	COOEt	H	105 (0.12)	1.4711	$C_{13}H_{20}O_4$	65.00	8.33	64.95	8.41
V[e]	$(CH_2)_4$	H	COOEt	H	127 (0.28)	1.4722	$C_{14}H_{22}O_4$	66.14	8.66	66.26	8.76
VI	$(CH_2)_6$	H	COOEt	H	149 (0.02)	1.4692	$C_{16}H_{26}O_4$	68.09	9.22	67.82	9.24
VII	$(CH_2)_8$	H	COOEt	H	164 (0.25)	1.4708	$C_{18}H_{30}O_4$	69.68	9.68	69.49	9.88
VIII	$(CH_2)_{12}$	H	COOEt	H	190 (0.14)[f]	1.4703	$C_{22}H_{38}O_4$	72.13	10.39	71.28	10.16
IX	$(CH_2)_{16}$	H	COOEt	H	197 (0.15)[f]	...	$C_{26}H_{46}O_4$	73.93	10.90	73.10	10.71
X		H	COOEt	H	153 (0.1)	1.4888	$C_{15}H_{22}O_4$	67.67	8.27	67.07	8.31
XI	$(CH_2)_3$	H	COOEt	Ph	156 (0.05)	1.5251	$C_{19}H_{24}O_4$	72.15	7.59	72.64	7.54
XII	OCH_2CH_2O	H	COOEt	H	158 (0.4)	1.4870	$C_{12}H_{18}O_6$	55.81	6.98	55.70	7.30
XIII[e]		COOET	COOEt	COOEt	...	...	...	...	...	...	...

[a] No particular configuration about the double bonds is implied by the way the general structure is depicted. [b] Usually a mixture of two or more of the possible isomers. [c] Infrared spectra of compounds I through XI were essentially identical with that of *trans*-ethyl crotonate in the olefin regions: N. B. Colthrup, *et al.*, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, p 250. [d] Prepared by Monsanto Research Corp., Dayton, Ohio, according to the method of G. P. Chiusoli and G. Cometti, *Chim. Ind.* (Milan), **45**, 401 (1963). [e] Taken from the preliminary communication (see ref 2). [f] A Kontes semi micro falling film apparatus was used for purification. The temperature and pressure cited represent the conditions under which the apparatus was used.

In this paper we wish to report that a variety of functionally substituted cyclic compounds may now be made by a new route, intramolecular electrolytic reductive coupling ("electrohydrocyclization," EHC). This method gives excellent results in the construction of three-, four-, five-, and six-membered carbocyclic rings from bisactivated olefins; it is applicable in the formation of certain heterocyclic systems; it permits an extension of the principles of reductive coupling with displacement[6] to intramolecular reaction; it may be used to prepare bicyclic compounds.

Results and Discussion

EHC of Bisactivated Olefins.—All the compounds of this category that were used in this investigation are given in Table I. The major subclass chosen for intensive study was in the ester series shown below



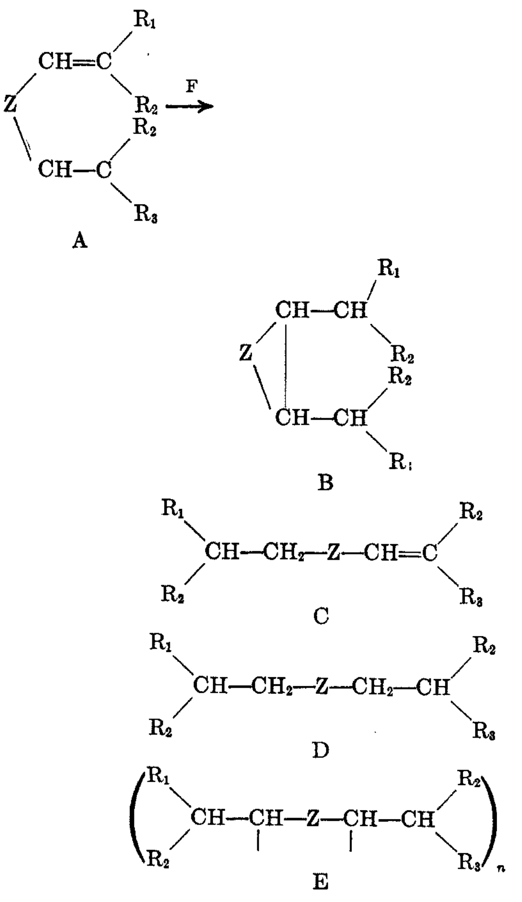
$$(CR_2)_n\begin{cases}CH{=}CHCOOEt\\CH{=}CHCOOEt\end{cases}$$

R = Et or H

because (a) it was not too difficult to obtain synthetically, (b) it permitted the study of the ease of formation of increasing ring sizes as one advanced through homologously related compounds, and (c) it yielded in many cases known products, a fact which assisted in the identification of the products obtained from the electrolyses.

The electrolytic reduction of a bisactivated olefin, A,[7] may lead to several products (Scheme I): the desired cyclized product B, the monoolefin C, the tetrahydro compound D, and oligomers E. The latter products are produced by intermolecular reductive coupling.

SCHEME I



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[6] Paper XI: M. M. Baizer, *J. Org. Chem.*, **31**, 3847 (1966).

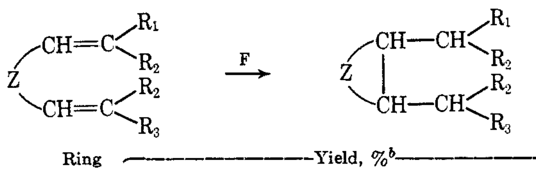
[7] See Table I for possible combinations of Z, R_1, R_2, and R_3.

Table II summarizes the results of the EHC of the bisactivated olefins described in Table I.

Several of the bisactivated olefins behaved in "normal" fashion and gave varying amounts of cyclized products, tetrahydro compounds, and oligomeric material (see Tables II and III for results and experimental details, respectively). These diolefins included diethyl 3,3-diethyl-2,5-heptadiene-1,7-dioate (I, *ca.* 60% conversion[8]), diethyl 2,6-octadiene-1,8-dioate (II, *ca.* 100% conversion[8]), and diethyl 2,7-nonadiene-1,9-dioate (IV, *ca.* 50% conversion[8]).

TABLE II

EHC OF BISACTIVATED OLEFINS[a]



	Ring	Yield, %[b]		
Diolefin	size formed	Cyclic compd	Tetrahydro compd	Oligomer
I	3	*Ca.* 98	...	?
I	4	41	48	10
III	4	15	...	Uncertain[c]
III	4	9[d]	...	Uncertain[c]
IV	5	*Ca.* 100	...	8
V[e]	6	90	...	9
V[e]	6	81	...	12
VI[f]	...	...	Small amount	Uncertain[g]
VI[h]	...	...	43	Uncertain[i]
VII[h]	...	...	50	Uncertain[i]
VIII[h]	...	...	72	Uncertain[i]
IX[h]	...	...	*Ca.* 100	...
X	5[j]	37[k]	26	?
XI	5	65	...	?
XII	6	89	...	...
XIII[e]	6	86	...	...

[a] See Table I for identification of Z, R_1, R_2, and R_3 shown in general reaction below. [b] Based on current input. [c] See paper XIV: J. P. Petrovich, J. D. Anderson, and M. M. Baizer, *J. Org. Chem.*, **31**, 3897 (1966). [d] This reaction is limited to vinyl ethers which do not contain aromatic groups bonded to the ether linkage: P. Given and M. E. Peover [*Nature*, **184**, 1064 (1959)] have demonstrated that carbon-oxygen bonds in aromatic compounds can be cleaved by electrochemical hydrogenolysis. We have found that ethyl β-phenoxyacrylate is cleaved electrochemically to phenol (unpublished work). [e] Data was taken from preliminary communication (see ref 2). [f] All of VI was in the electrolysis solution at the start of the experiment. [g] Although this was the major product of the reaction, the yield can not be determined with certainty as a mixture of oligomers was obtained with a range of molecular weights. [h] The diolefin added dropwise to the catholyte during the course of the experiment. [i] Once again the oligomeric material was a mixture, and thus a yield could not be calculated. [j] Could be visualized as a six-membered ring formation. [k] Gas evolution occurred from the cathode during most of the experiment. This led to a lower current efficiency.

Special mention should be made concerning the electrolyses of certain of the bisactivated olefins. 1,6-Dicyanohexadiene-1,5 (III) was very difficult to study owing to its tendency to polymerize. The mechanism of the polymerization is not understood and could be chemical (for example, hydroxide ion initiation) or electrochemical in nature or possibly a combination of both. The net effect of this polymerization is to reduce the amount of diolefin available for the EHC reaction, and thus the reported yield based on current input (see Table II) is undoubtedly artificially low. In order to minimize polymer formation—a bimolecular or higher order reaction—III was added to the catholyte dropwise during the electrolysis. Considerable amounts of oligomer were formed under these conditions. In another experiment run under the same conditions, except that the pH was maintained in the 5–6 range, the oligomeric material was substantially reduced. The yield of cyclic product was only 9% (based on current input), *but no acyclic reduced products* were found. Vigorous hydrogen evolution occurred throughout the course of this experiment which is expected when operating under acidic conditions. As a consequence, however, the current efficiency for the EHC reaction was extremely low. The yield of cyclic product was 43% based on conversion.

The electrolysis of *cis*-diethyl 1,3-cyclopentanediacrylate (X) gave *trans*-diethyl 2,3-norbornanediacetate, a product of transannular EHC, in 37% yield. Other products also found were (a) *cis*-diethyl 1,3-cyclopentanedipropionate (26%) and (b) a small amount of a high-boiling material believed to be oligomer.

The electrolysis of diethyl 2-phenyl-2,7-nonadiene-1,9-dioate (XI) resulted in an example of an intramolecular *mixed reductive coupling.*[9] The cyclic product, *cis*- and *trans*-diethyl α-phenyl-1,2-cyclopentanediacetate, was isolated in 65% yield. A small amount of a high-boiling material was also found which presumably was an oligomer. During the electrolysis a red color was observed[10] on the cathode surface which was undoubtedly due to the reactive intermediate formed. The mechanistic implications of this observation will be discussed subsequently.[11]

A further example[2] of the synthesis of heterocyclic systems was demonstrated by the EHC of 1,2-bis-(2-ethoxycarbonylvinyloxy)ethane (XII). The cyclic compound, 2,3-bis(ethoxycarbonylmethyl)-1,4-dioxane, was formed in 89% yield.[12]

The electrolyses of diethyl 2,10-dodecadiene-1,12-dioate (VI), diethyl 2,12-tetradecadiene-1,14-dioate (VII), diethyl 2,16-octadecadiene-1,18-dioate (VIII), and diethyl 2,20-docosanediene-1,22-dioate (IX) did not lead to the desired cyclic compounds. Mixtures of tetrahydro compounds and oligomers were obtained whose relative amounts depended on whether the total amount of diolefin was dissolved in the catholyte at the start of an electrolysis or was added dropwise during the course of an electrolysis (once again see Table II and Table III).

The mechanism of the EHC reaction has been the subject of intensive study.[11] Evidence obtained by the use of polarography and coulometry strongly suggests a concerted reductive process as depicted in Scheme II. The bisactivated olefin (F) participates in the concerted reductive ring closure in a one-electron-transfer step. This is followed by rapid protonation

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(8) This conversion was calculated assuming a two-electron reduction per mole of diolfin.

(9) The intermolecular reaction was first discussed in paper IV: M. M. Baizer, *J. Org. Chem.*, **29**, 1670 (1964).

(10) A similar coloration was noted during the electrolysis of 9-benzalfluorene. See paper VI: M. M. Baizer and J. D. Anderson, *ibid.*, **30**, 1348 (1965).

(11) See Table II, footnote *c*.

(12) See Table II, footnote *d*.

TABLE III

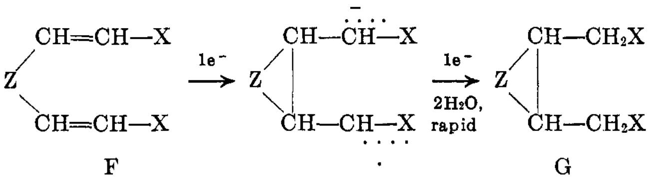
CATHOLYTE COMPOSITIONS AND ELECTROLYSIS PARAMETERS[a]

Diolefin	Method[b]	Catholyte compn: Diolefin, g	Salt,[c] g	Water, g	Cosolvent, g	Cathode voltage[d]	Av amp	Total amp-hr
I	A	41.0	26.9	10.0	CH_3CN, 70.7	−1.85	2.0	4.67
II	A	40.0	26.9	10.0	CH_3CN, 70.7	−1.95	2.5	7.62
III[e]	B	13.0	100.0	50.0	None	−2.10	0.5	5.60
III[f,g]	B	13.2	100.0	32.0	CH_3CN, 32.0	−1.92	3.0	17.08
IV	A	40.0	26.9	10.0	CH_3CN, 70.7	−1.98	2.0	4.50
VI[e]	A	40.0	26.9	10.0	CH_3CN, 70.7	−2.03	2.0	3.80
VI[f]	B	22.9	27.0	15.0	CH_3CN, 72.0	−2.21	1.5	6.20
VII	B	10.0	26.9	10.0	CH_3CN, 100.7	−2.21	1.5	2.16
VIII	B	25.0	27.0	15.0	CH_3CN, 100.0	−2.09	1.0	6.35
IX	B	15.0	30.0	5.0	CH_3CN, 120.0	−2.40	1.0	3.00
X	A	7.5	30.0	20.0	CH_3CN, 100.0	−2.02	0.3	1.91
XI	A	11.5	30.0	20.0	CH_3CN, 100.0	−1.98	0.5	2.10
XII	A	55.0	36.0	9.0	CH_3CN, 40.0	−2.04	2.0	5.25

[a] The temperature range for the experiments was 20–30°. The pH was maintained at 7–9 by the addition of acetic acid except where otherwise noted. [b] Method A: all of the diolefin was dissolved in the catholyte at the start of the electrolysis. Method B: the diolefin was added in a dropwise manner to the catholyte during the course of the electrolysis. [b] The salt was tetraethylammonium *p*-toluenesulfonate. [d] *Vs.* the saturated calomel electrode. [e] Experiment 1. [f] Experiment 2. [g] The pH was maintained in the 5–6 range.

and a further one-electron reduction giving the cyclic product (G).

SCHEME II

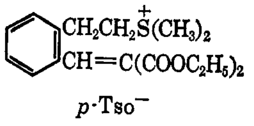


The observed limitations of the EHC reaction tend further to substantiate the concerted mechanism. The fact that diolefins VI–IX did not give the eight-, ten-, fourteen-, and eighteen-membered rings, respectively, would appear to rule out mechanisms such as the diradical coupling process associated with the acyloin reaction.[13]

The use of molecular models of bisactivated olefins can help to predict their utility for the EHC reaction. It was noted that models of I (the precursor to the cyclopropane ring) and IV (the precursor to the cyclopentane ring) can easily be oriented in such a way that the double bonds were parallel and the carbons β to the activating group were approximately one carbon–carbon bond distance apart.[14] Examination of the model of II (precursor to the cyclobutane ring) showed that the alignment described above could only be attained with steric strain.

EHC with Displacement.—One can visualize that compounds which contain individually both an electrocleavable group and a functional group which can serve as an acceptor site (*e.g.*, activated olefin) may undergo a cyclization by either of two sequences: (a) the site containing the "leaving group" is reduced first and the residual intermediate attacks the acceptor or (b) the acceptor site is reduced first and the resulting intermediate—now a donor—displaces the "leaving group." In both cases numerous competitive reactions may be anticipated.[6] An example of b was chosen for examination.

Dimethyl *o*-[(bis-β-ethoxycarbonyl)vinyl]phenethylsulfonium *p*-toluenesulfonate (XIV) was prepared by the sequence described in the Experimental Section.

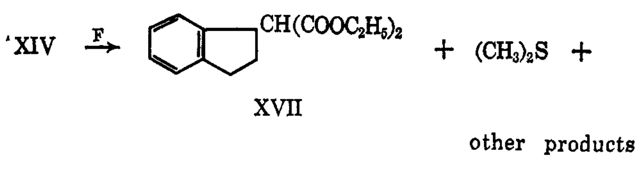


XIV

The polarogram of XIV in dimethylformamide (DMF) using tetrabutylammonium iodide as supporting electrolyte showed waves at −1.45 (sce)[15] and −1.72 v (sce), respectively. Under similar conditions diethyl benzalmalonate (XV) showed a first reduction wave at −1.53 v and dimethylphenethylsulfonium *p*-toluenesulfonate (XVI) showed a first wave at −1.84 and a second wave −2.55 v which was due to the styrene liberated by decomposition of XVI. It therefore appeared that XIV underwent reduction first at the double bond.

$$\underset{\text{XV}}{Ph—CH=C(COOC_2H_5)_2} \qquad \underset{\text{XVI}}{Ph—CH_2CH_2\overset{+}{S}(CH_3)_2—p\text{-}Tso^-}$$

Bulk electrolysis of XIV in DMF containing tetraethylammonium *p*-toluenesulfonate started at −1.32 v (sce); the cathode voltage slowly became more negative and ended at −2.21 v (sce). A 12.6% yield of crude product was obtained. The product, diethyl 3-indanylmalonate (XVII), was identified *via* vpc com-



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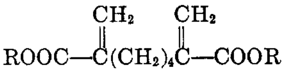
[13] This reaction is known to give high yields to macrocyclic rings; for a review, see S. M. McElvain, *Org. Reactions*, 4, 256 (1948).

[14] A model of the diolefin shows that it would fulfill these steric requirements and this should be a candidate for the EHC reaction. This would



$$ROOC—\overset{\overset{CH_2}{\|}}{C}(CH_2)_4\overset{\overset{CH_2}{\|}}{C}—COOR$$

permit the synthesis of an eight-membered ring, which was not possible using the diolefin VI.

[15] Saturated calomel electrode.

parison with an authentic sample.[16] The experiment also yielded considerable higher boiling material undoubtedly arising from competitive hydrodimerization, intermolecular displacements, etc. Repetition of the experiment using slow addition of XIV to the catholyte so that the cathode voltage was kept at −1.41 to −1.55 v (sce) did not improve the yield.

Experimental Section[17]

A. **Electrolysis Apparatus.**—This has been described previously.[18] A mercury cathode, area 55 cm^2, was used throughout.

B. **Analytical Instrumentation.**—The proton magnetic resonance (nmr) spectra were determined at room temperature on a Varian A-60 spectrometer. Spectro Grade chloroform and carbon tetrachloride were used as solvents and tetramethylsilane as the internal standard. The spectra of the samples were obtained in *ca.* 20% solution by volume.

The analytical vapor phase chromatography (vpc)[19] was conducted on an F & M 310. Three columns were used throughout the investigations: a 3-m 1% silver nitrate–18% Carbowax 20M on Chromosorb W column, a 3% DC550 on Teflon column, and a 20% XE-60 on Chromosorb W column. The silver nitrate–Carbowax column was used almost exclusively for product analyses from the electrolyses.

Preparative vpc collections were made using the F & M 770. A silver nitrate–Carbowax column of make-up similar to that described above was used.

C. **Preparation of Intermediate Materials and Bisactivated Olefins.** **γ,γ-Diethylpimelic Acid.**—The compound was prepared by the Wolf-Kishner reduction of **γ-acetyl-γ-ethylpimelic acid**[20] using a method similar to that described by Colonge and Vuillemet.[21]

1,14-Tetradecanedioic Acid.—The acid was prepared using a Kolbe electrolysis in the synthetic sequence. **Monomethyl suberate**[22] (282 g, 1.5 moles), sodium methoxide (*ca.* 0.1 mole), and 500 ml of absolute methanol were charged to an electrolysis cell equipped with a 4 × 5 cm smooth platinum anode and two 5.5 × 2.5 cm smooth platinum cathodes. The electrolysis was conducted at reflux temperature and at an average current of *ca.* 1.6 amp. Periodic current reversals were required to remove insoluble material from the electrode surfaces. The electrolysis was discontinued when the pH of the solution became greater than 7. The solution was then acidified with acetic acid after which all "volatile" materials were removed *in vacuo.* The residue was taken up in ether–benzene, the insoluble material was removed by filtration, and the filtrate was washed with sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed and the residue was recrystallized from methanol. **Dimethyl 1,14-tetradecanedioate** (225.7 g, 84.7% based on conversion) was obtained, mp 43–45° (lit.[23] mp 43–45°).

The dimethyl ester was saponified by refluxing with methanolic sodium hydroxide followed by acidification with hydrochloric acid. The crude acid was washed with copious amounts of water and dried *in vacuo.* **1,14-Tetradecanedioic acid** (127.6 g, 40%) was obtained, mp 123–124° (lit.[24] mp 122–123°).

1,18-Octadecanedioic Acid.—**Monomethyl sebacate**[22] was electrolyzed using a procedure similar to that described above to produce **dimethyl 1,18-octadecanedioate**, mp 55–56° (lit.[25] mp 56°). Saponification of the dimethyl ester gave the subject compound, mp 122–123° (lit.[25] mp 124.5°).

1,22-Docosanedioic Acid.—Electrolysis of **monomethyl dodecanedioate,**[26] using the procedure described above, gave **dimethyl 1,22-docosanedioate,** mp 67–69° (lit.[27] mp 69–70°). Saponification of this ester gave the subject acid, mp 126–128° (lit.[28] mp 125.6–126.8°).

***cis*-1,3-Cyclopentanedipropionic Acid.**—Sodium borohydride (19 g, 0.5 mole) was added under nitrogen at 0–5° to a solution of **2,5-cyclopentanonedipropionitrile** (96.7 g, 0.51 mole)[29] dissolved in 600 ml of acetonitrile. The reaction mixture was stirred in the cold for *ca.* 2 hr, warmed to room temperature, diluted with 2 l. of water, and extracted with methylene chloride. These extracts were back washed with water and dried over magnesium sulfate. Removal of the solvent gave 95 g (98%) of crude **2,5-cyclopentanoldipropionitrile.** Its infrared spectrum showed a strong band at 2.9 μ (OH) and the complete absence of a carbonyl absorption. The analytical sample, n^{25}_{D} 1.4850, was obtained by passing the crude material through a Kontes semi micro falling film apparatus at 207° (0.025 mm).

Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.75; H, 8.33; N, 14.58. Found: C, 68.82; H, 8.34; N, 14.33.

2,5-Cyclopentanoldipropionitrile (64.8 g, 0.34 mole) was treated with phosphorus tribromide (0.34 mole) in benzene–pyridine using standard organic techniques to give 35.1 g (41%) of crude **1-bromo-2,5-cyclopentanedipropionitrile.** The infrared spectrum showed no hydroxyl absorption. The material was unstable to distillation and was used in the crude form in the subsequent step.

The 35.1 g of crude 1-bromo-2,5-cyclopentanedipropionitrile was refluxed with 200 ml of dimethylformamide (DMF) for 4 hr.[30] **1,3-Cyclopent-1-enedipropionitrile** (14.5 g, 60%) was obtained, bp 122° (0.02 mm), n^{25}_{D} 1.4842.

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.86; H, 8.05; N, 16.09. Found: C, 75.43; H, 8.26; N, 15.91.

1,3-Cyclopent-1-enedipropionitrile (13.5 g, 0.08 mole), dissolved in 100 ml of glacial acetic acid, was mixed with 1 g of 10% palladium on carbon. Hydrogenation of the material was conducted in a Parr apparatus at an initial pressure of 32 psi. Hydrogen uptake (0.08 mole) was complete in 4 hr. After removal of solvent the crude hydrogenated material was heated under reflux for 24 hr in 100 ml of concentrated hydrochloric acid. Dilution with water followed by ether extraction gave 13.4 g (76% for two steps) of crude ***cis*-1,3-cyclopentanedipropionic acid,**[29] mp 96–97° after two recrystallizations from water (lit.[29] mp 98–99° after similar purification).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.68; H, 8.41. Found: C, 61.38; H, 8.35.

2-Phenylazelaic Acid.—Diethyl phenylmalonate (306.8 g, 1.3 moles) was added dropwise at 0–5° to a slurry of 55% sodium hydride–mineral oil (56.2 g, 1.3 moles) in 1 l. of DMF. When the hydrogen evolution had ceased, 7-bromoheptanonitrile (200 g, 1.1 moles) was added dropwise. An exothermic reaction ensued. The temperature rose to *ca.* 60°. The reaction mixture was then warmed on a steam bath for 6 hr. Dilution of the reaction mixture with water, followed by extraction with methylene chloride, drying, removal of solvent, and distillation of the residue gave 213.4 g (62%) of **diethyl phenyl 6-cyanohexylmalonate,** bp 192° (0.55 mm) to 198° (0.6 mm), n^{25}_{D} 1.4913.

Anal. Calcd for $C_{20}H_{27}NO_4$: C, 69.57; H, 7.83; N, 3.83. Found: C, 69.77; H, 7.85; N, 3.90.

The above intermediate (213 g, 0.62 mole) was heated at reflux for *ca.* 36 hr with 1 l. of concentrated hydrochloric acid. The acid was removed under vacuum and the residue was heated to 200° in a mineral oil bath to ensure complete decarboxylation. The crude product was recrystallized from water giving 89.6 g (55%) of **2-phenylazelaic acid,** mp 81.5–83° (lit.[31] mp 78–80°).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.18; H, 7.58. Found: C, 68.45; H, 7.42.

Synthesis of the Series of α,α'-Dibromo Diesters.[32]—The com-

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(16) M. Protiva, Z. J. Vejédek, and J. O. Jélek, *Collection Czech. Chem. Commun.*, **16**, 336 (1951).

(17) Boiling points are uncorrected.

(18) Paper I: M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

(19) Vpc integrated areas were used in all experiments to determine amounts of products and recovered starting material in the distillation cuts. In the cyclohexane case (electrolysis of V, see ref 2) the response of all components (products and starting material) was essentially linear. Linearity was assumed in all subsequent experiments.

(20) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942).

(21) J. Colonge and R. Vuillemet, *Bull. Soc. Chim. France*, 2235 (1961).

(22) Prepared according to the general procedure of S. Swann, Jr., *et al.*, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 276.

(23) H. Erdtman, *Acta. Chem. Scand.*, **2**, 209 (1948).

(24) R. G. Jones, *J. Am. Chem. Soc.*, **69**, 2350 (1947).

(25) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York, N. Y., 1957, p 940.

(26) Prepared using the general method of H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942).

(27) R. Signer and P. Sprecher, *Helv. Chim. Acta*, **30**, 1001 (1947).

(28) A. Kreuchunas, *J. Am. Chem. Soc.*, **75**, 3339 (1953).

(29) T. L. Westman and A. E. Kober, *J. Org. Chem.*, **29**, 2448 (1964).

(30) J. D. Anderson, submitted for publication.

(31) F. Salmon-Legagneur and J. Leoné, *Compt. Rend.*, **260**, 3681 (1965).

(32) The bisactivated olefins I–XI (with the exception of III) were prepared going through this class of compounds as intermediates.

TABLE IV

α,α'-DIBROMO DIESTERS

	$n^{25}D$	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Diethyl α,α'-dibromo-γ,γ-diethylpimelate	1.4910	$C_{15}H_{26}Br_2O_4$	44.33	6.40	44.37	6.54
Diethyl α,α'-dibromosuberate	1.4850	$C_{12}H_{20}Br_2O_4$	37.11	5.16	37.17	5.30
Diethyl α,α'-dibromoazelate	1.4842	$C_{13}H_{22}Br_2O_4$	38.81	5.22	38.59	5.41
Diethyl α,α'-dibromosebacate	1.4835	$C_{14}H_{24}Br_2O_4$	40.38	5.77	40.19	5.90
Diethyl α,α'-dibromododecanedioate	1.4815	$C_{16}H_{28}Br_2O_4$	43.24	6.31	43.07	6.44

pounds were prepared from the corresponding dicarboxylic acids according to the general method of Lüttringhaus and Merz.[33] Yields were generally *ca.* 80%. The dibromo diesters, which were purified by flash distillation at 200–225° (0.2 mm) using an Asco rotary film still, are listed in Table IV. The remaining compounds in this series were used in the crude form in subsequent reactions.

Syntheses of Bisactivated Olefins.—Table I gives the properties and analyses of the diolefins used in this study. The diolefins were prepared by the dehydrobromination of the corresponding α,α'-dibromo diesters[32] with DMF.[30] The example below is illustrative of the method.

A solution of 153.0 g of diethyl α,α'-dibromosebacate in 300 ml of DMF was refluxed for 5 hr. At the end of this period the reaction mixture was cooled to room temperature and diluted with 500 ml of water. The aqueous solution was extracted with ether. The extracts were combined, backwashed with water, and dried over magnesium sulfate. The ether was distilled off and the residue was distilled through a 1-ft Vigreux column. Distillation gave 63.1 g (68%) of **diethyl 2,8-decadiene-1,10-dioate** (V).

Vpc analysis of the material showed 2 peaks in an 18/82 ratio. Nmr analysis showed that the minor component was the *cis,trans* isomer and the major component the *trans,trans* isomer.

Synthesis of 1,2-Bis(2-ethoxycarbonylvinyloxy)ethane (XII).—There was added under nitrogen with stirring a solution of 6.2 g of ethylene glycol (0.1 mole) and 1.0 g of triethylenediamine, dissolved in 25 ml of dioxane, to a solution of 39.2 g of ethyl propiolate (0.4 mole), dissolved in 100 ml of dioxane. The addition was conducted in a dropwise fashion, maintaining the reaction temperature at 5° with an ice-salt-water bath. After the addition was complete, the reaction mixture was allowed to warm to room temperature. At this point the mixture was taken up in benzene, washed with dilute hydrochloric acid, sodium bicarbonate solution, and water until neutral, and dried over magnesium sulfate. After evaporation of solvent, the reaction mixture was distilled through a 2-ft Vigreux column giving 13.4 g (52%) of product.

D. Electrolyses of Bisactivated Olefins. General Procedure.—The catholyte composition and electrolysis parameters for each bisactivated olefin studied in this paper are summarized in Table III. The anolyte was a 50% aqueous tetraethylammonium *p*-toluenesulfonate solution in all cases.

On completion of an electrolysis the catholyte was diluted with water and extracted with either ether or methylene chloride. After drying and removal of solvent the residue was either distilled using a semimicro vacuum-jacketed distillation column or, if a solid, it was recrystallized. Vpc analyses of the distillation cuts, isolation of the pure components *via* preparative vpc, and subsequent use of analytical data were used in the product identification. These product identifications are detailed below.

Product Identifications from the Electrolysis of I.—The reaction mixture (36.2 g) was distilled giving four fractions: (1) bp 118–122° (0.4 mm), 7.4 g; (2) bp 124–125° (0.4 mm), 9.7 g; (3) bp 125–129° (0.4 mm), 15.8 g; and (4) bp 130° (0.5 mm), 1 g. A residue (1.1 g) remained. Fractions 1–4 contained three components (A, B, and C) in varying amounts. A and B were identified as *cis*- and *trans*-diethyl 3,3-diethyl-1,2-cyclopropanediacetate. Mass spectrographic analyses of both peaks (collected using a vpc capillary column) gave parent ions at *m/e* 270 (theoretical 270) and the following fragmentation pattern: *m/e* 225 (loss of OC_2H_5), *m/e* 197 (loss of $COOC_2H_5$), and *m/e* 183 (loss of $CH_2COOC_2H_5$).

A sample of A was collected *via* preparative vpc, $n^{25}D$ 1.4462.

Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.67; H, 9.63. Found: C, 66.87; H, 9.74.

The nmr spectrum of A showed it to be the *cis* isomer. The δ values and intensities of the signals are given: a triplet at −0.61 (ring protons), a multiplet at *ca.* −1.20 (ethyl group protons), and a triplet at −1.23 ($OCCH_3$) for a total of 18.6 H, a doublet at −2.28 (3.92 H, CH_2CO), and a quartet at −4.05 (4.00 H, OCH_2C). The nmr spectrum of *ca.* a 50–50 mixture of A and B gave a more complex spectrum with the ring protons and methylene protons in the acetate side chains split into complex multiplets. This indicates that B is the *trans* isomer as its spectrum should be more complex than that of the *cis* isomer.

C was identified as recovered diolefin by comparison of vpc retention times. The residue was not analyzed, but by analogy with other systems it could be an oligomer of I.

Converting the vpc data to grams gave the following amounts which correspond to a nearly quantitative yield based on current input: 11.3 g (0.042 mole) of *cis*- and 12.1 g (0.044 mole) of *trans*-cyclopropanediacetate.

Product Identifications from the Electrolysis of II.—The reaction mixture (38.3 g) was distilled giving six fractions: (1) bp 88° (0.3 mm), (2) bp 79–82° (0.12 mm), (3) bp 84–88° (0.12 mm), (4) bp 86–94° (0.12 mm), (5) bp 100–132° (0.19 mm), and (6) bp 132° (0.19 mm). The residue from the distillation weighed 7.1 g. Three components (A,[34] B, and C) were found in the fractions. Fraction 1 contained only A and B and fraction 2 was pure C.

A was identified as a mixture of *cis*- and *trans*-diethyl 1,2-cyclobutanediacetate by analyses of a sample collected *via* vpc. Mass spectrographic analysis of A showed a parent ion at *m/e* 228 (theoretical 228) and fragments at *m/e* 183 (loss of OC_2H_5), *m/e* 155 (loss of $COOC_2H_5$), and *m/e* 141 (loss of $CH_2COOC_2H_5$). The nmr spectrum of A was consistent with the cyclobutane derivative. The δ values and intensities of the signals follow: a triplet at −1.23 (6.2 H, $OCCH_3$), a set of multiplets from −1.45 to −2.10 (ring protons) and a set of multiplets from −2.10 to −2.95 (CH_2CO) for a total of 10.2 H, and a quartet at −4.07 (4.0 H, OCH_2C).

Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.16; H, 8.77. Found: C, 63.35; H, 8.92.

Component B was identified as diethyl suberate by comparison of vpc retention times with an authentic sample. Pure B, collected *via* vpc, was hydrolyzed to suberic acid, mp 140–141° (lit.[35] mp 139–141°).

Component C was identified *via* vpc as recovered II.

The residue was a dimer of II showing unsaturation in the infrared spectrum. The structure was tentatively formulated as $(EtOOCCH{=}CH(CH_2)_2\underset{|}{C}HCH_2COOEt)_2$.

Anal. Calcd for $C_{24}H_{38}O_8$: C, 63.44; H, 8.37; mol wt, 454. Found: C, 63.35; H, 8.81; mol wt (benzene), 460.

The yields of products using the vpc data were 41% *cis*- and *trans*-cyclobutanediacetate (13.4 g, 0.059 mole) and 48% diethyl suberate (7.9 g, 0.034 mole).

Product Identifications from the Electrolyses of III. Experiment 1.—Distillation of the reaction mixture gave 4.7 g of distillate, bp 94° (0.02 mm) to 110° (0.1 mm), and a residue weighing 7.0 g. The distillate contained four components (A, B,[34] C, and D).

Components A, C, and D were identified as recovered isomers of III by vpc retention time comparisons and by mass spectrograph analysis which showed parent ions of *m/e* 132 (theoretical 132). Component B was analyzed by mass spectrograph and a parent ion of *m/e* 134 (theoretical 134 for 1,2-cyclobutanediacetonitrile) was found.

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

[34] A mixture of two components inseparable under the vpc conditions used.

[35] J. Cason, L. Walleave, and C. Whiteside, *J. Org. Chem.*, **14**, 41 (1949).

Converting the vpc data to grams gives 2.1 g (15%) of a mixture of *cis*- and *trans*-1,2-cyclobutanediacetonitrile.

The *residue* showed unsaturation in the infrared spectrum. The molecular weight was roughly a multiple of four units of III.

Anal. Found: C, 70.68; H, 7.57; N, 19.29; O, 1.63;[36] mol wt (chloroform), 430.

Experiment 2.—Vpc data indicated a 9% yield of 1,2-cyclobutanediacetonitrile. Identification was obtained by vpc comparison with material from experiment 1 (see above).

Product Identifications from the Electrolysis of IV.—The reaction mixture (37.4 g) was distilled giving five fractions: (1) bp 101–105° (0.5 mm), 0.8 g; (2) bp 105–108° (0.5 mm), 11.5 g; (3) bp 108–112° (0.5 mm), 5.8 g; (4) bp 114° (0.5 mm), 8.1 g; and (5) bp 98–106° (0.13 mm), 7.4 g. The residue after distillation weighed 3.2 g. Four components (A, B, C, and D) were found in the fractions *via* vpc. Fractions 1 and 2 contained only A, B, and C.

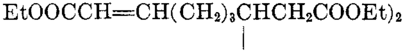
Components A and B were identified as *trans*- and *cis*-diethyl 1,2-cyclopentanediacetate, respectively. A mixture containing 81% A and 19% B was collected *via* vpc.

Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.42; H, 9.16. Found: C, 64.59; H, 9.24.

Mass spectrograph analysis of the above mixture gave a parent ion at *m/e* 242 (theoretical 242) and fragments at *m/e* 197 (loss of OC_2H_5), *m/e* 168 (loss of $COOC_2H_5$), and *m/e* 155 (loss of $CH_2COOC_2H_5$).

For the assignment of the isomers a pure sample of A was collected *via* vpc, n^{25}_{D} 1.4483 (lit.[37] n^{25}_{D} 1.4477 for the *trans* isomer). The nmr spectrum of this sample gave the following signals with their δ values and intensities: a triplet at −1.25 ($OCCH_3$) and a series of multiplets from −0.8 to −2.0 (ring protons) for a total of 14.24 H, a multiplet at *ca.* −2.3 (4.16 H, CH_2CO), and a quartet at −4.06 (4.00 H, OCH_2C).

Components C and D were identified as the two isomers of IV. The residue analyzed as a dimer of IV. Unsaturation bands were present in the infrared spectrum. The structure was formulated as



$(EtOOCCH{=}CH(CH_2)_3CHCH_2COOEt)_2$.

Anal. Calcd for $C_{26}H_{42}O_8$: C, 64.73; H, 8.71; mol wt, 482. Found: C, 64.04; H, 8.42; mol wt (benzene), 454.

Calculating the amount of product from the vpc data gave 16.0 g (0.066 mole) of *trans*- and 4.7 g (0.019 mole) of *cis*-cyclopentanediacetate. The combined yield was *ca.* 100% based on current input.

Product Identifications from the Electrolyses of VI. Experiment 1.—The distillation of the electrolysis reaction mixture gave a distillate of 11.9 g, bp 111° (0.5 mm) to 150° (0.25 mm), and a high-boiling residue, 23.8 g. The distillate contained a small amount of diethyl dodecanedioate (vpc analysis and comparison with an authentic sample) but was mostly recovered VI. The residue was undoubtedly a mixture of oligomers of VI as the molecular weight, 754 in chloroform, was not a multiple of the molecular weight of the diolefin.

Experiment 2.—The reaction mixture was distilled giving 12.7 g of material, bp 116° (0.12 mm) to 152° (0.15 mm), and a residue, 4.8 g. Vpc analysis of the distillate and comparison of components with authentic samples gave 7.3 g (43%) of diethyl dodecanedioate, a small amount of a product not identified, and recovered VI. The residue, molecular weight of 652 in benzene, is believed to be a mixture of oligomers of VI.

Product Identifications from the Electrolysis of VII.—The reaction mixture (9.6 g) gave 2.4 g of distillate, bp 150° (0.45 mm) to 160° (0.25 mm) and 6.4 g of a high-boiling residue. Vpc analysis of the distillate showed 1.5 g (0.015 mole, 50%) of diethyl tetradecanedioate by comparison with an authentic sample along with recovered VII. The residue, which presumably was a mixture of oligomers of VII, had a molecular weight of 726 (in benzene).

Product Identifications from the Electrolysis of VIII.—The reaction mixture (27.4 g) gave 18.4 g of distillate. The fraction boiling at 171–179° (0.12 mm) was pure diethyl octadecanedioate, mp 42°. The structure was verified by a mixture melting point (no depression) and vpc retention time comparison with an authentic sample. Vpc analysis of the distillate showed a total of 16.0 g (0.043 mole, 72%) of diethyl octadecanedioate. The remaining material was recovered VIII.

The residue (4.8 g) from the above distillation had an average molecular weight of 855 (in benzene), indicating it to be a mixture of oligomers of VIII.

Product Identifications from the Electrolysis of IX.—The reaction mixture (*ca.* 14 g) solidified on standing. The solid was recrystallized from petroleum ether (bp 30–60°) giving 11.8 g (*ca.* 100%) of diethyl docosanedioate, mp 55–57° (lit.[38] mp 56°).

Product Identifications from the Electrolysis of X.—Distillation of the reaction mixture gave four fractions: (1) bp 116° (0.05 mm), 1.5 g; (2) bp 116° (0.05 mm) to 120° (0.03 mm), 3.1 g; (3) bp 121–131° (0.025 mm), 1.2 g; and (4), bp 132–155° (0.025 mm), 0.5 g. A nondistillable residue (0.8 g) was also obtained. Four components (A, B, C, and D) were detected *via* vpc analysis. Fraction 1 was mostly A.

Pure A was collected *via* preparative vpc and was identified as *trans*-diethyl 2,3-norbornanediacetate, n^{25}_{D} 1.4640. Mass spectrograph analysis gave a parent ion at *m/e* 268 (theoretical 268) and fragments at *m/e* 223 (loss of OC_2H_5), *m/e* 195 (loss of $COOC_2H_5$), *m/e* 181 (loss of $CH_2COOC_2H_5$), and also at *m/e* 166, 152, 93, and 88. Nmr analysis gave a very complex spectrum. Assigning the CH_2 group (from $COOCH_2C$) an integral of 4 H, a total integration of 24.2 H was obtained (theoretical 24 H).

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.16; H, 8.95. Found: C, 67.02; H, 8.95.

Hydrolysis of A gave *trans*-2,3-norbornanediacetic acid, mp 170° (lit.[39] mp 169° for *trans* isomer).

Essentially pure B was collected and identified as *cis*-diethyl 1,3-cyclopentanedipropionate, n^{25}_{D} 1.4542. Mass spectrograph analysis showed a parent ion at *m/e* 270 (theoretical 270) and fragments at *m/e* 225 (loss of OC_2H_5), *m/e* 197 (loss of $COOC_2H_5$), *m/e* 183 (loss of $CH_2COOC_2H_5$), and also at *m/e* 180, 109, and 95.

Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.67; H, 9.63. Found: C, 66.62; H, 9.69.

Components C and D were identified as recovered isomers of X. The residue was not characterized.

Using vpc data of the four fractions the following yields were obtained: 3.6 g (0.013 mole, 37%) of the norbornanediacetate and 1.4 g (0.005 mole, 26%) of the cyclopentanedipropionate.

Product Identifications from the Electrolysis of XI.—Distillation of the reaction mixture gave 9.1 g of a fraction, bp 140–144° (0.07 mm), n^{25}_{D} 1.5015, containing *cis*- and *trans*-diethyl α-phenyl-1,2-cyclopentanediacetate and also gave a residue (1.3 g). Mass spectrograph analysis of the fraction gave no parent but gave fragments at *m/e* 273 (loss of OC_2H_5), *m/e* 245 (loss of $COOC_2H_5$), and *m/e* 164 (rearrangement ion produced from H migration to give $PhCH_2COOC_2H_5$). The nmr spectrum of the fraction showed the δ values and intensities of the signals given below: a triplet at −1.17 ($OCCH_3$), a series of multiplets from *ca.* −1.4 to −1.9 (ring protons) and a series of multiplets from *ca.* −1.9 to −2.4 (CH_2COOR) for a total of 15.61 H, a multiplet at *ca.* −3.26 (1.3 H, $PhC\mathit{H}COOR$), a quartet at −4.00 (3.95 H, OCH_2C), and a multiplet at −7.23 (5.29 H, aromatic protons).

Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.70; H, 8.18. Found: C, 71.80; H, 8.30.

The residue was a mixture of recovered XI and a high-boiling material not characterized.

The yield of the cyclopentanediacetate (0.025 mole) was 65%.

Product Identification from the Electrolysis of XII.—Distillation of the reaction mixture gave several fractions, one of which was identified as pure 2,3-bis(ethoxycarbonylmethyl)-1,4-dioxane, bp 113° (0.29 mm), n^{25}_{D} 1.4520. Vpc analysis of all of the fractions showed 23.0 g (89%) of the product.

Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.38; H, 7.69. Found: C, 54.82; H, 7.70.

Mass spectrograph analysis gave a parent ion at *m/e* 260 (theoretical 260) and a fragmentation pattern consistent with 1,4-dioxane compounds. Nmr analysis of the product gave a spectrum with the following δ values and signal intensities: a triplet at *ca.* −1.2 (6.02 H, $OCCH_3$), a degenerate doublet at −2.3 (3.99 H, side-chain methylene H), a multiplet at *ca.* −3.6 (ring protons), and a quartet at −4.0 (OCH_2C) for a total of 9.96 H.

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(36) This oxygen content corresponds to *ca.* one oxygen per tetramer unit. This finding suggests that an oxygenated species is responsible for initiation of the oligomerization.

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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), $n^{23.5}\mathrm{D}$ 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**, $n^{24}\mathrm{D}$ 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), $n^{23.5}\mathrm{D}$ 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**, $n^{24}\mathrm{D}$ 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, $n^{23}\mathrm{D}$ 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), $n^{23}\mathrm{D}$ 1.5031.

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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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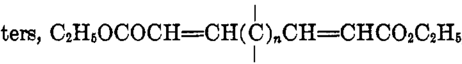
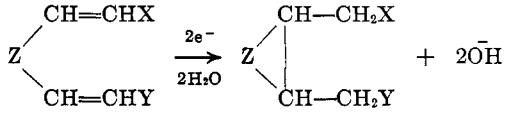
A polarographic study of the esters,  $C_2H_5OCOCH{=}CH(\overset{|}{\underset{|}{C}})_nCH{=}CHCO_2C_2H_5$, showed that those members of this series (n = 1–5) which formed cyclic compounds on macroelectrolysis characteristically reduced more easily than model monoolefins, $C_2H_5OCO(CH_2)_5CH{=}CHCO_2C_2H_5$ 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



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

work an apparently new polarographic phenomenon, the positive shift of cathode potential associated with a concerted reduction/carbon–carbon bond formation,

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