buret. The rate of addition was such that a maximum current of 0.6 A was passed. The electrolysis was discontinued when the current had fallen to 0.05 A. For cie experiments 0.07 mol of the olefin was taken up in acetonitrile (total volume of 25 ml) and the solution was added to the catholyte at a rate equivalent to 5.6×10^{-3} mol/hr with a syringe pump. A constant current of 0.3 A was maintained [*i.e.*, 0.3 A = (53.6 A hr/mol)(5.6×10^{-3} mol/hr)]. The catholyte was continuously saturated with CO_2 during the electrolyses. The cathode potential was monitored with a sce.

General Electrolysis Procedure. Monocarboxylation. The apparatus employed is shown in Figure 3. The top layer of propionitrile [0.06 *M* in $(C_4H_9)_4N^+BF_4^-$ and 2.8 *M* in H_2O] was circulated through the cell while being saturated with 100% CO_2 for 15 min prior to starting the electrolysis. Acrylonitrile was then added at a rate of 2.43 g/hr to the circulating propionitrile electrolyte solution (continuous CO_2 saturation). A constant current of 2.35 A was maintained [*i.e.*, 2.35 A = (53.6 A hr/mol)(4.38×10^{-2} mol/hr)].

Work-Up and Analyses of Catholytes. The products of electrocarboxylation under anhydrous conditions were converted to their methyl esters by treating the catholyte solution directly with an excess (0.28 mol) of methyl iodide at ice-bath temperatures (*cf.* footnote *c* of Table II). The acetonitrile and excess methyl iodide were removed and the organic products were separated from the electrolyte by benzene–water extraction. If authentic samples were available, analyses were done directly on the benzene-soluble material by glc (internal standards), using one of the following columns and conditions: (a) 6 ft × 0.125 in. S.S. 3% OV-101 on Chromosorb W (80–100 mesh), 150 → 280° at 10°/min; (b) 10 ft × 0.125 in. S.S. 5% FFAP + 1% Carbowax 20M on Chromosorb G (80–100 mesh), 100 → 200° at 10°/min; (c) 10 ft × 0.125 in. S.S. 3% QF-1 on Gas Chrom Q (60–80 mesh), 100 → 200° at 10°/min. Products for which authentic samples were not available were isolated by distillation and/or preparative glc. The following column and conditions were used: 3 ft × 0.75 in. S.S. 30% FFAP + 6% Carbowax 20M on Chromosorb W (60–80 mesh), 200°. The products so obtained were subsequently used for yield determinations by glc (internal standards). Yield data for electrocarboxylations under partially aqueous conditions were obtained by analyzing the aqueous extract by nmr using sodium acetate as an internal standard.

Identification of Products. Products were confirmed by comparing their glc retention lines, mass spectra, nmr spectra, and boiling points. New compounds were identified by their mass spectra, nmr spectra, and elemental analyses. These compounds and the appropriate analytical data are given in Table III.

Acknowledgment. The authors wish to thank Gary Dinkelkamp for his technical assistance.

Registry No.—Carbon dioxide, 124-38-9.

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Electrocarboxylation. II.[1] Electrocarboxylative Dimerization and Cyclization

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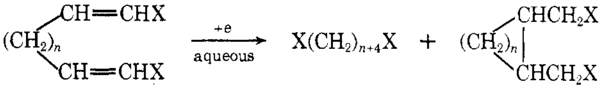
The competitive reactions of electrochemically generated anion radicals of activated olefins with carbon dioxide and unreduced activated olefins have been studied. Dimethyl maleate and carbon dioxide are converted to 1,1,2,3,4,4-hexasubstituted butane derivatives *via* dimerization of electrochemically generated intermediates. Methyl acrylate and carbon dioxide are converted to 1,1,4,4-tetrasubstituted derivatives. The observed product is consistent with a pathway involving reaction of the uncarboxylated methyl acrylate anion radical with unreduced methyl acrylate followed by carboxylation. Electrocarboxylation of the bisactivated olefins, $CH_3O_2CCH{=}CH(CH_2)_nCH{=}CHCO_2CH_3$, gave a variety of cyclic and acyclic products. The influence of *n* on the product distribution and the mechanistic implications are discussed.

Conditions favorable for the conversion of activated olefins to dicarboxylated monomers have been described previously.[1] At low concentrations of unreduced olefin relative to dissolved carbon dioxide, it was shown that carbon dioxide effectively competes with unreduced olefin as an electrophile toward the activated olefin anion radical.

Under aqueous conditions various types of intra- and intermolecular interactions (*i.e.*, couplings) have been observed when activated or bisactivated olefins are electrochemically reduced.[2] Simple activated olefins are converted to acyclic dimeric products, while bisactivated olefins are converted to combinations of dihydro and cyclic products (eq 1).



$$(CH_2)_n\left\langle\begin{matrix}CH{=}CHX\\ CH{=}CHX\end{matrix}\right. \xrightarrow[\text{aqueous}]{+e} X(CH_2)_{n+4}X + (CH_2)_n\left\langle\begin{matrix}CHCH_2X\\ |\\ CHCH_2X\end{matrix}\right. \qquad (1)$$

$n = 2$–4

$X = CO_2C_2H_5$, CN

Table I
Polarographic Behavior of Activated Olefins in the Presence and Absence of Dissolved Carbon Dioxide[a]

Olefin	$-E_{1/2}$ (sce)[b]	n (N_2)[c]	n (CO_2)
Dimethyl maleate	1.53	1	1
	1.84		1
Methyl acrylate	2.10	1	2
Dimethyl 2,6-octadiene-1,8-dioate, $n = 2$	2.24	1	
Dimethyl 2,7-nonadiene-1,9-dioate, $n = 3$	2.12	1	*d*
Dimethyl 2,8-decadiene-1,10-dioate, $n = 4$	2.24	1	

[a] Polarographic solutions 0.1 *M* in $(C_2H_5)_4N^+OTs^-$ in CH_3CN with olefin 10^{-3} *M* and CO_2 10^{-3} *M* by saturation with 1% $CO_2(N_2)$ mixture. [b] $E_{1/2}$ *vs.* saturated calomel electrode (sce). Values reported for nitrogen saturated solutions. A slight positive shift was observed when recording polarograms in CO_2 solution. [c] The approximate number of faradays consumed per mole of substrate is given by *n*. This value was obtained by comparison of diffusion currents and in some cases confirmed by coulometry. [d] Broad wave obscured by CO_2 reduction wave (ca. −2.3 v).

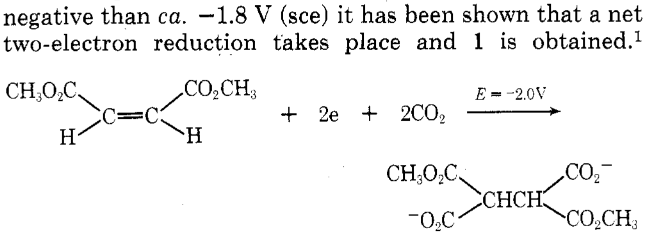
Carboxylative dimerizations have been reported previously by Wawzonek.[3] However, these studies described the reduction of olefins in the presence of carbon dioxide under noncontrolled conditions. The work reported here (1) describes the use of potential control in directing electrocarboxylation toward either monomer dicarboxylation or electrocarboxylative dimerization, (2) examines the influence of excess olefin on the electrocarboxylation process as well as the probable pathway by which dimeric products are obtained, and (3) compares the behavior of bisactivated olefins under carboxylation conditions to that observed in electrolyses under aqueous conditions.

Results and Discussion

Polarography. The polarographic behavior of the activated olefins subsequently subjected to bulk electrolysis is shown in Table I.

Bulk Electrolyses. General Comments. Product yields are expressed as current efficiencies. Assuming the absence of nonelectrochemical routes to the products reported, this number represents the minimum yield based on starting material. All major products detected were identified and are described below. Some loss of products probably occurred by electromigration of carboxylate ion from the cathode to the anode during the electrolysis. Attempts were made to minimize this by adding excess electrolyte to the anode compartment. No attempts were made to obtain material balances.

Radical Carboxylate Dimerization. The polarogram of dimethyl maleate in the presence of carbon dioxide reveals two plateaus (Figure 1). At cathode potentials more negative than *ca.* −1.8 V (sce) it has been shown that a net two-electron reduction takes place and 1 is obtained.[1]



$$\mathrm{CH_3O_2C{-}CH{=}CH{-}CO_2CH_3} + 2e + 2CO_2 \xrightarrow{E\,=\,-2.0\mathrm{V}} \mathrm{(CH_3O_2C)(^-O_2C)CHCH(CO_2^-)(CO_2CH_3)}$$

1

Based on the polarogram it should be possible by proper potential control to generate the radical carboxylate and obtain products derived from subsequent reaction of the radical. This was confirmed by electrolyzing a solution of dimethyl maleate and carbon dioxide at a controlled potential (Hg) of −1.65 V (sce) which gave, after esterification, hexamethyl 1,1,2,3,4,4-butanehexacarboxylate (2) in 46% current efficiency.

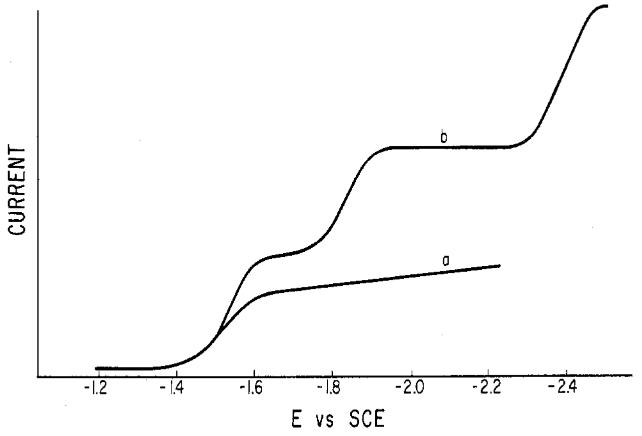
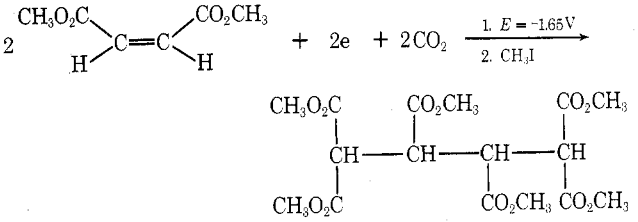


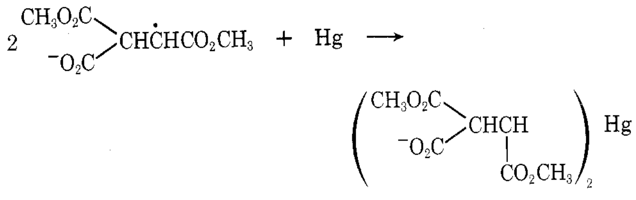
Figure 1. Polarogram of (a) dimethyl maleate in acetonitrile containing 0.1 *M* tetraethylammonium tosylate saturated with nitrogen and (b) replacing nitrogen with 1% carbon dioxide–nitrogen mixture.



$$2\,\mathrm{CH_3O_2C{-}CH{=}CH{-}CO_2CH_3} + 2e + 2CO_2 \xrightarrow[\text{2. CH}_3\text{I}]{\text{1. }E\,=\,-1.65\mathrm{V}} \mathrm{(CH_3O_2C)_2CH{-}CH(CO_2CH_3){-}CH(CO_2CH_3){-}CH(CO_2CH_3)_2}$$

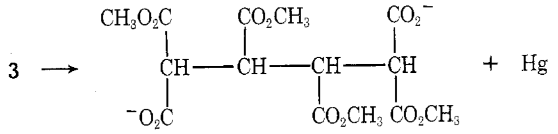
2

Although radical intermediates generated at mercury cathodes often form mercurials,[4] the absence of colloidal mercury in the catholyte is sufficient evidence to eliminate involvement of mercury in the coupling reaction. Thus, there is no significant contribution from the reaction followed by disproportionation of 3 to 4 and mercury.



$$2\,\mathrm{(CH_3O_2C)(^-O_2C)\dot{C}HCHCO_2CH_3} + \mathrm{Hg} \longrightarrow \mathrm{\left((CH_3O_2C)(^-O_2C)CHCH(CO_2CH_3)\right)_2Hg}$$

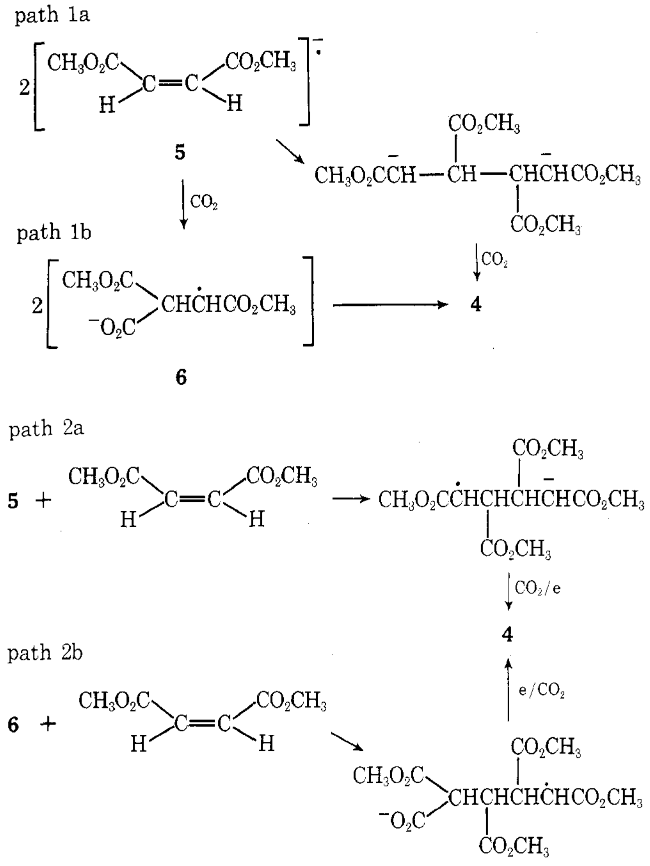
3



$$\mathbf{3} \longrightarrow \mathrm{(^-O_2C)(CH_3O_2C)CH{-}CH(CO_2CH_3){-}CH(CO_2CH_3){-}CH(CO_2CH_3)(CO_2^-)} + \mathrm{Hg}$$

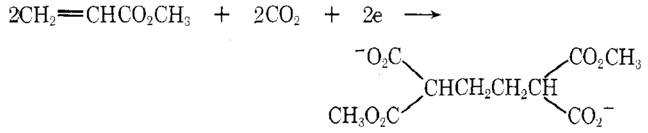
4

Several pathways to 2 can be considered. As suggested by Bard in his studies on the electrochemistry of diactivated olefins,[5] the anion radical of dimethyl maleate (5) dimerizes to the dianion, which is then carboxylated (path 1a). A related sequence (path 1b) involves dimerization of the radical carboxylate (6). Alternatively, dimeric products are obtained by reaction of either 5 or 6 with unreduced maleate, followed by reduction and carboxylation (path 2). A series of electrolyses with varying initial concentrations of dimethyl maleate showed no variations in yield of 4 (Table II, 2 = 4 as its methyl ester). This eliminates reaction sequences in which unreduced dimethyl maleate participates and, thus, leaves path 1 as the most likely route to dimeric products.



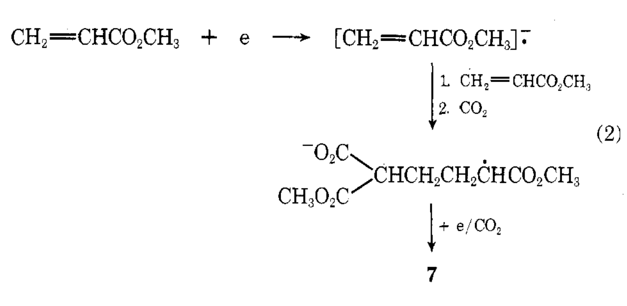
Olefin Anion Radical Reactions. Olefin and Carbon Dioxide Competition. The reaction of olefin anion radicals with carbon dioxide results in products in which carbon dioxide has been added to each of the olefinic carbon atoms.[1] As the concentration of unreduced olefin in the catholyte is increased, a point should be reached at which it competes effectively with carbon dioxide as an electrophile for the anion radical. The polarographic behavior of monoactivated olefins in the presence of carbon dioxide (*i.e.*, a single two-electron wave) does not allow one to predict products expected or the sequence by which they are formed under these conditions.

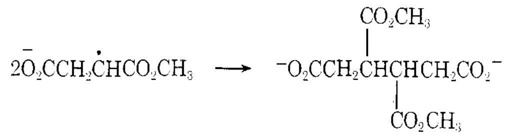
A series of experiments in which mixtures of methyl acrylate and carbon dioxide were electrolyzed (Table III) indicates that the primary product of electrocarboxylative dimerization of monoactivated olefins is a 1,1,4,4-tetrasubstituted butane derivative (7).



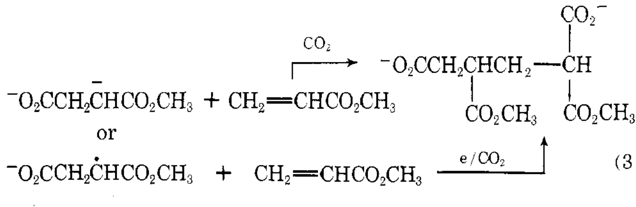
7

Variations of the relative amounts of acrylate and carbon dioxide are consistent with the following pathway to 7 (eq 2). The reduction in current efficiency to dimeric products with decreasing concentrations of methyl acrylate supports the contention that the products of electrohydrodimerization of similar substrates under aqueous conditions involve reactions of the olefin anion radical with unreduced olefin.[6] In contrast to the results with dimethyl maleate, there is no evidence for dimerization of either the acrylate anion radical or the radical carboxylate. The latter is supported by the observation that no 1,2,3,4-tetrasubstituted butane derivatives are observed, *i.e.*,

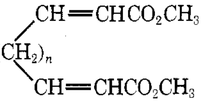




Of minor importance is the following (eq 3), based on the small amounts of tetramethyl 1,1,3,4-butanetetracarboxylate detected.



Electrocarboxylative Cyclizations. Upon reduction the bisactivated olefins (8) may be expected to undergo a variety of electrocarboxylative reactions. In the simplest



8 (n = 2-4)

Table II
Bulk Electrolyses of Dimethyl Maleate and Carbon Dioxide at Various Initial Maleate Concentrations[a]

[Maleate]	Yield, % (ce)[b]
0	44
0.14	42
0.31	46
0.62	41

[a] Electrolyte solution 0.25 M $(C_2H_5)_4N^+OTs^-$ in CH_3CN with CO_2 saturation (1 atm), −20°. Cathode potential controlled at −1.65 V (sce). Portionwise addition of 2.9 g (0.02 mol) of maleate at total current passed of 0.02 faraday. [b] **4** → **2** with methyl iodide [J. H. Wagenknecht, M. Baizer, and J. L. Chruma, *Syn. Commun.*, **2,** 215 (1972)]; yields expressed as current efficiencies (ce) assuming a 2-faraday reduction per mole of product.

Table III
Electrocarboxylative Dimerization of Methyl Acrylate[a]

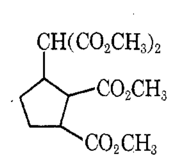
Initial [acrylate], M	Current density, mA/cm^2	Yield, % (ce),[b] X = CO_2CH_3 X_2CH-CH_2X	X_2CHCH_2-$CHXCH_2X$	$X_2CH(CH_2)_2$-CHX_2
0	20	61	None	None
0.33	20	29	5	28
1.32	20	8	5	47

[a] Electrolyte solution 0.25 M $(C_2H_5)_4N^+OTs^-$ in CH_3CN with $[CO_2]$ 0.1 M. All but [acrylate] = 0 run at controlled current to less than 20% conversion. Run at [acrylate] = 0 made at controlled potential (−2.1 V) with portionwise addition of acrylate (ref 1). [b] Carboxylate salts converted to methyl esters with methyl iodide [J. H. Wagenknecht, M. M. Baizer, and J. L. Chruma, *Syn. Commum.*, **2,** 215 (1972)]; yields expressed as current efficiencies assuming a 2-faraday reduction per mole of product.

case, each end of the molecule acts independently with the formation of products arising from the successive dicarboxylation of the two activated olefin moieties. However, as the molecular conformations of either the starting materials or reaction path intermediates are altered by variations in *n* of **8**, intramolecular interactions will compete with carboxylation in much the same way as intermolecular interactions compete with carboxylation in the cases of dimethyl maleate and methyl acrylate described above.

Dimethyl 2,6-Octadiene-1,8-dioate (8, *n* = 2). Electrocarboxylation of a solution of 8 ($n = 2$) gave, after esterification with methyl iodide, dimethyl [2,3-bis(methoxycarbonyl)cyclopentyl]malonate (**9**). No other cyclic or acyclic products were detected.

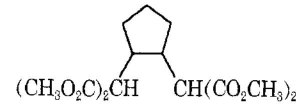
$$\underset{\mathbf{8}\ (n=2)}{CH_3O_2CCH{=}CHCH_2CH_2CH{=}CHCO_2CH_3} \xrightarrow[2.\ CH_3I]{1.\ e/CO_2}$$



9, 72%

Dimethyl 2,7-Nonadiene-1,9-dioate (8, *n* = 3). Electrocarboxylation of a solution of 8 ($n = 3$) gave, after esterification with methyl iodide, tetramethyl 1,2-cyclopentylenedimalonate (**10**). No acyclic products were detected.

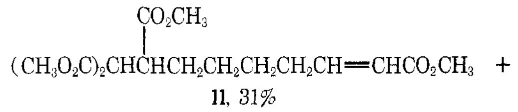
$$\underset{\mathbf{8}\ (n=3)}{CH_3O_2CCH{=}CHCH_2CH_2CH_2CH{=}CHCO_2CH_3} \xrightarrow[2.\ CH_3I]{1.\ e/CO_2}$$



10, 50%

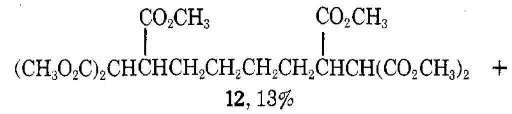
Dimethyl 2,8-Decadiene-1,10-dioate (8, *n* = 4). Electrocarboxylation of a solution of 8 ($n = 4$) gave, after esterification with methyl iodide, a mixture of tetramethyl-1,1,2,8-octene-7-tetracarboxylate (**11**), hexamethyl 1,1,2,7,8,8-octanehexacarboxylate (**12**), and tetramethyl 1,2-cyclohexylenedimalonate (**13**).

$$\underset{\mathbf{8}\ (n=4)}{CH_3O_2CCH{=}CHCH_2CH_2CH_2CH_2CH{=}CHCO_2CH_3} \xrightarrow[2.\ CH_3I]{1.\ e/CO_2}$$



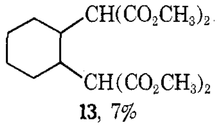
$$(CH_3O_2C)_2CH\overset{CO_2CH_3}{\overset{|}{C}H}CH_2CH_2CH_2CH_2CH{=}CHCO_2CH_3 \; +$$

11, 31%



$$(CH_3O_2C)_2CH\overset{CO_2CH_3}{\overset{|}{C}H}CH_2CH_2CH_2CH_2\overset{CO_2CH_3}{\overset{|}{C}H}CH(CO_2CH_3)_2 \; +$$

12, 13%



13, 7%

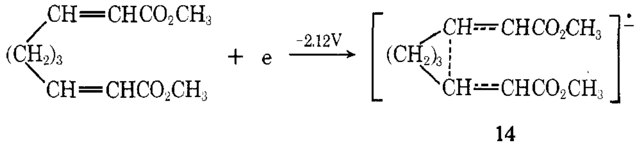
Table IV summarizes the results of the electrohydrocyclization of the same series of bisactivated olefins under aqueous conditions (*cf.* eq 1).[7]

With the exception of dimethyl 2,7-nonadiene-1,9-dioate (**8**, $n = 3$), the behavior of these olefins differs markedly under the two sets of conditions. The similarity in behavior for 8 ($n = 3$) can be attributed to the intramolecular interaction between the two olefin moieties in the sequence. Thus, the first electrode intermediate formed is one in which reduction and cyclization are concerted.[2b,7] This is reflected by a lower reduction potential for this compound (Table I). Subsequent carboxylations and reduction of **14** leads to the product observed. This sequence is analogous to that in which methyl acrylate is carboxylatively dimerized to a tetrasubstituted 1,1,4,4-butane derivative (eq 2).

Table IV
Electrohydrocyclization of Bisactivated Olefins[a]

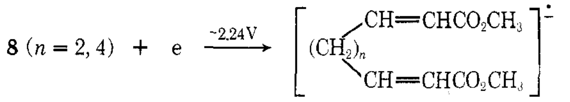
Olefin (8)	Yield, % (ce) Cyclic	Yield, % (ce) Acyclic
$n = 2$	41	48
$n = 3$	100	
$n = 4$	81–90	

[a] As their ethyl esters. Solvent–electrolyte 50% aqueous $(C_2H_5)_4N^+OTs^-$ at Hg.

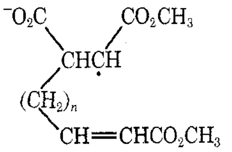


14

Dimethyl 2,6-octadiene-1,8-dioate (**8**, $n = 2$) and dimethyl 2,8-decadiene-1,10-dioate (**8**, $n = 4$) do not show a polarographic shift indicative of a concerted reduction–ring closure (Table I). Consequently, an acyclic anion radical intermediate (**15**) is formed at the electrode. Under aqueous conditions this intermediate is sufficiently long-lived (with respect to protonation) so that ring closure to intermediates of the general type **14** occurs to an appreciable extent. However, in the presence of carbon dioxide, **15** must be carboxylated at a rate exceeding that of ring closure, with the radical carboxylate (**16**, $n = 2, 4$) being formed. The conformation of **16** ($n = 2$) (as the radical or anion after reduction) is such that ring closure *via* a 1,5-interaction now occurs more rapidly than carbon dioxide incorporation to give, after esterification, **9**. A similar interaction occurs to a minor extent in the carboxylative dimerization of methyl acrylate (eq 3). The rate of closure of **16** ($n = 4$) is sufficiently slow (1,7-interaction required), so that the major products (**11** and **12**) are acyclic.



15 ($n = 2, 4$)



16 ($n = 2, 4$)

In conclusion, a variety of inter- and intramolecular interactions have been observed when mono-, di-, and bisactivated olefins are reduced in anhydrous media containing dissolved carbon dioxide. The following summarizes the types of reactivity observed.

(1) Activated olefins exhibiting two distinct one-electron waves in the presence of carbon dioxide are converted to highly substituted adipic acids *via* the dimerization of radical carboxylates provided that the potential is controlled on the plateau of the first wave.

(2) Activated olefins exhibiting a single two-electron wave in the presence of carbon dioxide are converted to α,α'-substituted adipic acids provided that the concentration of unreduced olefins is high relative to that of carbon dioxide. Under these conditions the unreduced olefin com-

Table V
Nmr and Mass Spectral Data

Compd[a]	Nmr, δ, ppm[b]	Mass spectrum,[c] m/e
Hexamethyl 1,1,2,3,4,4-butanehexacarboxylate (**2**)	4.1 (1 H, d, CHX_2)[d] 3.78 (3 H, s, OCH_3) 3.7 (6 H, s, OCH_3) 3.4 (1 H, d, CHX)[d]	342 ($M^+ - 2CH_3OH$) 314 [$M^+ - (CH_3OH + HCO_2CH_3)$] 283 [$M^+ - (2\ CH_3OH + CO_2CH_3)$] 282 [$M^+ - (2CH_3OH + HCO_2CH_3)$] 244 [$M^+ - (2CH_3OH + 2CO_2CH_3)$]
Tetramethyl 1,1,3,4-butanetetracarboxylate	3.79 (6 H, d, OCH_3)[e] 3.75 (3 H, s, OCH_3) 3.73 (3 H, s, OCH_3) 2.73 (3 H, m, CH_2X, CHX)[f] 2.23 (2 H, m, CH_2)	259 [$M^+ - CH_3O$) 227 [$M^+ - (CH_3O + CH_3OH)$] 199 [$M^+ - (CH_3OH + CO_2CH_3)$]
Dimethyl [2,3-bis(methoxycarbonyl)cyclopentyl]malonate (**9**)	3.78 (6 H, d, OCH_3)[e] 3.73 (3 H, s, OCH_3) 3.69 (3 H, s, OCH_3) 2.67 (2 H, m, CHX)[f] 1.85 (4 H, m, CH_2)	285 ($M^+ - CH_3O$) 284 ($M^+ - CH_3OH$) 256 ($M^+ - CO_2CH_3$) 253 [$M^+ - (CH_3O + CH_3OH)$] 224 [$M^+ - (CH_3OH + HCO_2CH_3)$] 196 ($M^+ - 2HCO_2CH_3$) 185 [$M^+ - HC(CO_2CH_3)_2$] 125 $\{M^+ - [HCO_2CH_3 + HC(CO_2CH_3)_2]\}$
Tetramethyl 1,2-cyclopentylenedimalonate (**10**)	3.80 (12 H, s, OCH_3) 3.75 (2 H, d, CHX_2)[f] 2.17 (2 H, m, CH) 1.87 (6 H, m, CH_2)	299 ($M^+ - CH_3O$) 267 [$M^+ - (CH_3O + CH_3OH)$] 235 [$M^+ - (CH_3O + 2CH_3OH)$] 199 [$M^+ - HC(CO_2CH_3)_2$] 167 $\{M^+ - [CH_3OH + HC(CO_2CH_3)_2]\}$ 166 [$M^+ - (CH_3OH + Z)$][h] 139 [$M^+ - (CO_2CH_3 + Z)$]
Tetramethyl 1,1,2,8-octene-7-tetracarboxylate (**11**)	7.17 (1 H, m, olefin) 5.95 (1 H, m, olefin) 3.79 (3 H, s, OCH_3) 3.75 (6 H, d, OCH_3)[e] 3.74 (3 H, s, OCH_3) 3.22 (1 H, m, CHX)[f] 2.23 (2 H, m, CH_2Y)[g] 1.49 (6 H, m, CH_2)	313 ($M^+ - CH_3O$) 285 ($M^+ - CO_2CH_3$) 280 ($M^+ - 2CH_3OH$) 248 ($M^+ - 3CH_3OH$) 221 [$M^+ - (2CH_3OH + CO_2CH_3)$]
Hexamethyl 1,1,2,7,8,8-octanehexacarboxylate (**12**)	3.81 (6 H, s, OCH_3) 3.77 (12 H, d, OCH_3)[e] 3.22 (2 H, m, CHX)[f] 1.42 (8 H, m, CH_2)	431 ($M^+ - CH_3O$) 403 ($M^+ - CO_2CH_3$) 398 ($M^+ - 2CH_3OH$) 371 [$M^+ - (CH_3O + CO_2CH_3)$] 366 ($M^+ - 3CH_3OH$) 331 [$M^+ - HC(CO_2CH_3)_2$] 307 [$M^+ - (3CH_3OH + CO_2CH_3)$] 299 ($331 - CH_3OH$) 267 $\{M^+ - [2CH_3OH + HC(CO_2CH_3)_2]\}$ 259 [$M^+ - (CHX_2CH_2X)$][f]

[a] Satisfactory C, H analyses were obtained. [b] Solvent $CDCl_3$ with TMS internal standard. [c] By direct probe or glc–mass spectrum, no molecular ions observed. [d] $X = CO_2CH_3$, $J = 10$ Hz. [e] Nonequivalent CO_2CH_3, separation *ca.* 1 Hz. [f] $X = CO_2CH_3$. [g] Y = olefin. [h] $Z = (HO)(CH_3O)C{=}C(H)(CO_2CH_3)$.

petes with carbon dioxide as an electrophile in the trapping of the activated olefin anion radical.

(3) Bisactivated olefins are electrocarboxylated, the products obtained being a function of the methylene chain length [**8** (n = 2–4)]. Intramolecular interactions are observed for **8** (n = 2, 3). The ends of the molecule act independently for **8** (n = 4).

Experimental Section

Equipment. The electrolysis system and instrumentation were the same as those described previously.[1]

Reagents and Starting Materials. Reagent grade acetonitrile (less than 80 ppm water) was obtained from Matheson Coleman and Bell and used without further purification. Methyl acrylate and dimethyl maleate were obtained from commercial sources. They were redistilled and stored with a trace of hydroquinone added. Dimethyl 2,6-octadiene-1,8-dioate [**8**, n = 2, bp 137° (0.6 mm)], dimethyl 2,7-nonadiene-1,9-dioate [**8**, n = 3, bp 126° (0.25 mm)], and dimethyl 2,8-decadiene-1,10-dioate [**8**, n = 4, bp 128° (0.25 mm)] were prepared by the method described previously for the corresponding ethyl esters.[7] Tetraethylammonium p-toluenesulfonate (Aldrich) was recrystallized several times from acetone and dried in a vacuum oven. The carbon dioxide was "bone dry" grade.

Reference Compounds. The preparations of trimethyl 1,1,2-ethanetricarboxylate and tetramethyl 1,1,2,2-ethanetetracarboxylate have been described previously.[1] Tetramethyl 1,1,4,4-butanetetracarboxylate (**7** as its methyl ester, mp 77°) was prepared as described in the literature.[8] Tetramethyl 1,2,3,4-butanetetracarboxylate[9] (mp 60° from methanol–petroleum ether) was obtained by the transesterification (methanol-p-toluenesulfonicacid) of the corresponding ethyl ester prepared by the electrohydrodimerization of diethyl maleate.[10] Tetramethyl 1,1,3,4-butanetetracarboxylate, bp 160° (1 mm), was prepared by the base-catalyzed addition of dimethyl malonate to dimethyl itaconate in a manner similar to that described for the corresponding ethyl ester.[11] Relevant analytical data are given in Table V.

General Electrolysis Procedure. The electrolyte solution [0.25 M $(C_2H_5)_4N^+OTs^-$ in acetonitrile] was added to the cell containing the Hg cathode and a properly positioned sce. In addition, 20 g of $(C_2H_5)_4N^+Cl^-$ and 10 ml of 1-octene were added to the anode compartment to provide a sacrificial anode reaction (*i.e.*, $Cl^- - e \rightarrow \frac{1}{2}Cl_2$). The cell and its contents were cooled to the desired temperature while the solution was saturated for 15 min with 100% CO_2.

Dimethyl Maleate and Methyl Acrylate. The electrocarboxylation of these olefins at initial [olefin] = 0 were done under controlled-potential conditions of −1.65 and −2.1 V, respectively. The olefin, dissolved in acetonitrile, was gradually added to the catholyte. The cell temperature was maintained at −20° for the maleate reduction and at 0° for the acrylate reduction. Electrolyses in which $[\text{olefin}] \neq 0$ were run to less than 20% conversion of the initial activated olefin charged to the catholyte so as not to significantly lower the olefin concentration below its desired initial concentration in the cell. A constant-current power supply was employed for these electrolyses.

Bisactivated Olefins. A solution of the olefin (0.015 mol) in acetonitrile was gradually added to the catholyte while potentiostating at −2.2 V (sce). The electrolyses were discontinued when the final current had decayed to the background current observed for carbon dioxide reduction.

Work-Up and Analysis of Catholyte. The products of electrocarboxylation were converted to their methyl esters by treatment with excess methyl iodide (*cf.* footnote *b* of Table II). The acetonitrile and excess methyl iodide were removed and the organic products were separated from the electrolyte by benzene–water extraction. If authentic samples were available, analyses were done directly on the benzene-soluble material by glc (internal standards or known addition methods) using either a 6 ft × 0.125 in. S.S. 3% OV-101 on Chromosorb W (80–100 mesh) or 8 ft × 0.125 in. S.S. 3% OV-17 on Gas-Chrom Q (60–80 mesh) column. Products for which authentic samples were not available were isolated and characterized as described below. Products so obtained were subsequently used for yield determinations by glc.

Isolation and Identification of Products. The relevant analytical data for new compounds obtained during this study are shown in Table V.

Hexamethyl 1,1,2,3,4,4-Butanehexacarboxylate (2). The residue from the benzene extract of the dimethyl maleate electrolysis was taken up in hot methanol; **2** (mp 136–137°) precipitated upon cooling.

Dimethyl [2,3-bis(methoxycarbonyl)cyclopentyl]malonate (9) was isolated by column chromatography (neutral Al_2O_3–benzene) of the benzene-soluble products obtained from the electrolysis of dimethyl 2,6-octadiene-1,8-dioate (**8**, $n = 2$). Attempts to distil the viscous product resulted in decomposition.

Tetramethyl 1,2-cyclopentylenedimalonate (10) was separated from the starting material by column chromatography (neutral Al_2O_3–*benzene) of the benzene-soluble residue obtained from* the electrolysis of dimethyl 2,7-nonadiene-1,9-dioate (**8**, $n = 3$). Attempts to distil the viscous product resulted in decomposition.

Hexamethyl 1,1,2,7,8,8-octanehexacarboxylate (12) was isolated as a solid by treating the benzene-soluble residue from the electrolysis of dimethyl 2,8-decadiene-1,10-dioate (**8**, $n = 4$) with ice-cold ether (mp 136–137° from methanol).

Tetramethyl 1,1,2,8-Octene-7-tetracarboxylate (11). The ether-soluble residue remaining after precipitation of **12** was adsorbed onto a column of neutral Al_2O_3. Benzene elution gave unreduced **8**, ($n = 4$) and **11**, respectively; **11** is a viscous liquid which decomposed upon attempted distillation.

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Registry No.—**2**, 40853-30-3; **8** ($n = 2$), 4756-84-7; **8** ($n = 3$), 52002-95-6; **8** ($n = 4$), 52002-96-7; **9**, 52002-97-8; **10**, 52002-98-9; **11**, 52002-99-0; **12**, 52003-00-6; dimethyl maleate, 624-48-6; methyl acrylate, 96-33-3; tetramethyl 1,1,3,4-butanetetracarboxylate, 52003-01-7.

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Reactivity of Benzo[*b*]thiophene in Electrophilic Reactions as Determined from Solvolysis Rates[1]

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Electrophilic replacement constants, σ_{Ar}^+, have been obtained for all positions of benzo[*b*]thiophene. The σ_{Ar}^+ values were defined from rate constants for the solvolysis of the six isomeric 1-(benzo[*b*]thienyl)ethyl chlorides in 80% ethanol–water. The positional order of reactivity in the benzo[*b*]thiophene ring was determined to be 3 > 2 > 6 > 5 > 4 > 7. All positions are more reactive than benzene.

Recent studies in these laboratories have determined relative reactivities of several heteroaromatic systems in an "electrophilic side-chain reaction,"[3] the solvolysis of 1-arylethyl derivatives.[4-7] A correspondence between solvolytic reactivity and reactivity in electrophilic aromatic substitutions is expected because of the similar electron deficiency developed in the aromatic system in the two types of reactions. In this paper we extend our studies of side-chain reactivity to the benzo[*b*]thiophene ring system and compare the results to literature data concerning the reactivity of benzo[*b*]thiophene in electrophilic reactions.

Aromatic reactivity data can be conveniently generalized by defining σ_{Ar}^+ values for use in the modified Hammett equation introduced by Brown.[8] For the particular electrophilic reaction being considered, a ρ value for the reaction is established from the rate data for substituted benzenes and then σ_{Ar}^+ constants are defined for aromatic systems from rate data obtained under the same conditions. We refer to σ_{Ar}^+ values as "replacement σ^+ values"[9] or "electrophilic replacement constants," rather than "substituent constants," because they signify replacement of the entire benzene ring by another aromatic system instead of the substitution of the aromatic system for one of the phenyl hydrogens. In addition to our studies,[4-7] this approach has been applied to aromatic hydrocarbons by Streitwieser,[10] and to heteroaromatic systems by Hill, *et al.*,[11] by Taylor,[12] by Marino,[13] and by Baker, Eaborn, and Taylor.[14]