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Electrocarboxylation. I.[1] Mono- and Dicarboxylation of Activated Olefins

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Short-lived ($t_{1/2} < 10^{-3}$ sec) anion radicals of activated olefins ($CH_2{=}CHX$ with X = CO_2CH_3, CN, and acetyl) generated at a mercury cathode under anhydrous conditions react rapidly with carbon dioxide. Further reduction of the radical carboxylate intermediate and subsequent carboxylation results in the formation of substituted succinic acid derivatives. An alternate pathway involves electroreduction of carbon dioxide and subsequent reactions of $CO_2{\cdot}^-$ with unreduced olefin. Under partially aqueous conditions the radical carboxylate intermediate is again formed. However, in the presence of water the anion formed by subsequent reduction of the radical carboxylate reacts preferentially with water. For example, acrylonitrile is converted to 3-cyanopropionic acid. The polarographic behavior of activated olefins in the presence and absence of dissolved carbon dioxide is compared with the products obtained upon bulk electrolysis of activated olefins in the presence of carbon dioxide.

Electrochemical syntheses involving activated olefins have been discussed previously.[2] Two types of behavior are observed, and conditions can be chosen such that one or the other behavior dominates. Electrolysis of activated olefins in aqueous electrolyte solutions at cathodes of low hydrogen overvoltage results in dihydro product. At cathodes

$$CH_2{=}CHX + 2e + 2H_2O \longrightarrow CH_3CH_2X + 2OH^-$$

$$X = \text{electron-withdrawing group}$$

of high hydrogen overvoltage in the presence of aqueous tetraalkylammonium salts, products of electrohydrodimerization are formed. In addition to quenching anionic inter-

$$2CH_2{=}CHX + 2e + 2H_2O \rightarrow X(CH_2)_4X + 2OH^-$$

mediates with water as above, there are several reports in the literature in which carbon dioxide is used as a trapping agent in order to demonstrate the existence of anionic intermediates generated by the electroreduction of neutral organic substrates in anhydrous media.[3]

The work reported here was designed to probe the synthetic utility of reducing activated olefins in the presence of carbon dioxide and to understand the extent to which the behavior under these conditions could be related to the known electrochemistry of activated olefins under aqueous conditions in the absence of carbon dioxide. This paper describes in detail the electrochemical behavior of activated olefins in the presence of dissolved carbon dioxide in both nonaqueous and partially aqueous systems under conditions favoring mono- or dicarboxylation. A subsequent paper[4] describes the electrocarboxylation of activated olefins under conditions favoring either intramolecular cyclization or intermolecular dimerization followed or accompanied by carboxylation.

Results and Discussion

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

A rapid reaction of the olefin anion radical[5] with carbon dioxide is clearly indicated by a doubling of the diffusion current when carbon dioxide is added to the electrolyte solution at a concentration equivalent to that of the olefin. This is illustrated for a typical monoactivated olefin in Figure 1, in which the polarograms of methyl acrylate in the presence and absence of carbon dioxide are shown. Interaction of the methyl acrylate anion radical generated at the electrode with carbon dioxide diffusing toward the electrode causes the diffusion current for carbon dioxide to be reduced by approximately one-half of the value observed in the absence of a reducible substrate (curves b and c). Thus, less carbon dioxide is available for polarographic reduction.

The pathway most consistent with the polarographic results is as follows.

$$CH_2{=}CHX + e \xrightarrow{E_{1/2}^{\,1}} [CH_2{=}CHX]^{\overset{\cdot}{-}}$$

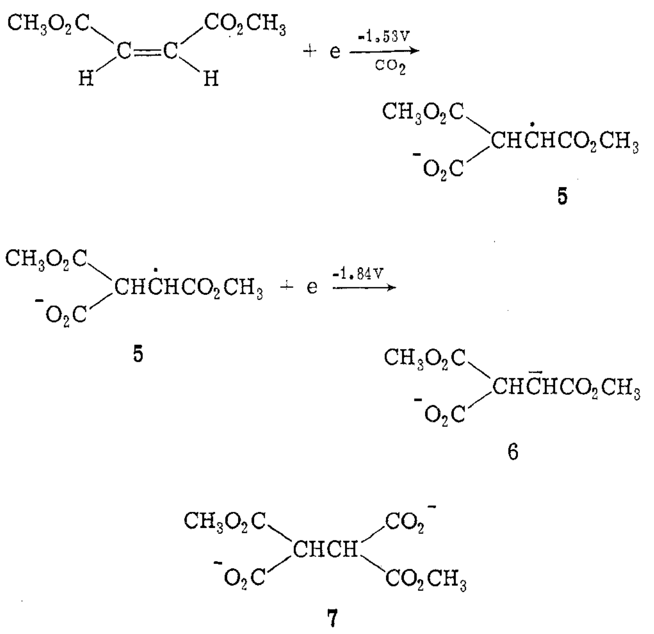
$$\underset{\mathbf{1}}{[CH_2{=}CHX]^{\overset{\cdot}{-}}} + CO_2 \longrightarrow \underset{\mathbf{2}}{{}^-O_2CCH_2\dot{C}HX}$$

$$\underset{\mathbf{2}}{{}^-O_2CCH_2\dot{C}HX} + e \xrightarrow{E_{1/2}^{\,2}} \underset{\mathbf{3}}{{}^-O_2CCH_2\bar{C}HX}$$

$$\underset{\mathbf{3}}{{}^-O_2CCH_2\bar{C}HX} + CO_2 \longrightarrow \underset{\mathbf{4}}{{}^-O_2CCH_2CHXCO_2^-}$$

$$X = CO_2CH_3,\ C(O)CH_3,\ CN$$

Reaction of **1** with carbon dioxide sufficiently disperses the charge in **2** so that the reduction of **2** to **3** can occur (*i.e.*, $|E_{1/2}^{\,2}| \leq |E_{1/2}^{\,1}|$). A lower limit for the value of $E_{1/2}^{\,2}$ of approximately −1.84 V (sce) is suggested from the data for the reduction of dimethyl maleate (Figure 2). In the presence of carbon dioxide, dimethyl maleate is reduced to its anion radical [$E_{1/2}^{\,1} = -1.53$ V (sce), $n = 1$] which reacts with carbon dioxide to form the radical carboxylate (**5**). The radical carboxylate (**5**) is stable toward further reduction at this potential, and subsequent reduction of **5** to the carbanion carboxylate (**6**) does not occur until −1.84 V (sce). Reaction of **6** with carbon dioxide gives the ethanetetracarboxylate derivative (**7**). Macroscale electrolyses of



dimethyl maleate on the plateau of the first wave and subsequent reaction of the radical carboxylate (**5**) are treated in the following paper.[4] Electrolyses on the plateau of the second wave are discussed below.

Bulk Electrolyses. Anhydrous. A series of electrolyses (Hg pool) was carried out under anhydrous conditions in order to confirm the polarographic interpretation of the behavior of activated olefins at low concentrations in the presence of dissolved carbon dioxide. Olefins showing distinct polarographic waves were electrolyzed under controlled potential conditions at a cathode voltage corresponding to the plateau of the reduction wave. The olefin was added in portions to the cathode compartment of the cell so as to maintain a concentration of unreduced olefin in the cell of less than 0.05 *M*. Carbon dioxide was continuously bubbled (1 atm) into the catholyte through a gas dispersion tube. Some of the olefins studied undergo reduction at potentials more negative than that of carbon dioxide. In these cases the electrolyses were run at a constant current with a constant rate of addition of olefin. The rate of addition was selected so as to correspond to the current selected, assuming a two-electron reduction of olefin. The results are presented in Table II.

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

Olefin	Registry no.	$-E_{1/2}$ (sce)[b]	n (N_2)[c]	n (CO_2)
Methyl acrylate	96-33-3	2.10	1	2
Methyl methacrylate	80-62-6	2.27	1	*d*
Methyl crotonate	18707-60-3	2.41	1	*d*
Methyl *trans*-β-methoxyacrylate	5788-17-0	2.67	1	*d*
Dimethyl maleate	624-48-6	1.53	1	1
		1.84		1
Acrylonitrile	107-13-1	2.14	1	2
Methacrylonitrile	126-98-7	2.31	1	*c*
Methyl vinyl ketone	78-94-4	1.91	1	2

[a] Polarographic solutions 0.1 *M* $(C_2H_5)_4N^+OTs^-$ 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 solution. A slight positive shift (*ca.* 0.05 V) 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] Wave obscured by CO_2 reduction wave which occurs at *ca.* −2.3 V (sce).[1]

Product yields are expressed as current efficiencies. Assuming the absence of nonelectrochemical routes to the products reported in the table, this number represents the minimum yield based on starting material. Under controlled potential conditions (cpe), minor amounts of dimeric carboxylates were observed.[4] No other major products were detected. Under controlled current conditions (cie), major products observed included oxalic and cyanoacetic acid derivatives. The former arises from reductive coupling of carbon dioxide and the latter from solvent carboxylation.[1] Both products reduce the current efficiency to observed products but not necessarily the chemical yield. Because of the low levels (*i.e.*, 0.05 *M*) at which the electrolyses were carried out, no attempt was made to obtain material balances. Some loss of products probably occurred by electromigration of the products (*i.e.*, dicarboxylate ion) from the cathode to the anode during the electrolysis. Attempts were made to minimize this by adding excess electrolyte to the anode compartment.

Olefins having reduction potentials distinctly separate from that of carbon dioxide (cpe in Table II) give products

Table II
Bulk Electrolyses of Activated Olefins in the Presence of Dissolved Carbon Dioxide[a]

Olefin	$-E_{1/2}$ (sce)	Control[b]	Product[c]	Yield, (ce)[d]
Methyl acrylate	2.10	cpe	Trimethyl 1,1,2-ethanetricarboxylate	61
Methyl methacrylate	2.27	cie	Trimethyl 1,2,2-propanetricarboxylate	42
Methyl crotonate	2.41	cie	Trimethyl 1,1,2-propanetricarboxylate	38
Methyl *trans*-β-methoxyacrylate	2.67	cie	Trimethyl 2-methoxy-1,1,2-ethanetricarboxylate	10
Dimethyl maleate	1.84	cpe (second wave)	Tetramethyl 1,1,2,2-ethanetetracarboxylate	31
Acrylonitrile	2.14	cpe	Dimethyl 2-cyanosuccinate	41
Methacrylonitrile	2.31	cie	Dimethyl 2-methyl-2-cyanosuccinate	28
Methyl vinyl ketone	1.91	cpe	Methyl levulinate	22
			Dimethyl 2-acetylsuccinate	16

[a] Electrolyte solution 0.25 *M* $(C_2H_5)_4N^+OTs^-$ in CH_3CN with CO_2 saturation (1 atm) at a Hg pool. [b] cpe = controlled potential electrolysis, cie = controlled current electrolysis (cathode potential = −2.15 V). [c] Catholyte solution treated with methyl iodide to convert tetraethylammonium carboxylates to methyl esters for isolation and characterization: J. H. Wagenknecht, M. M. Baizer, and J. L. Chruma, *Syn. Commun.*, 2 215 (1972). [d] Yields expressed as current efficiencies (ce), assuming a 2-faraday reduction per mole of product.

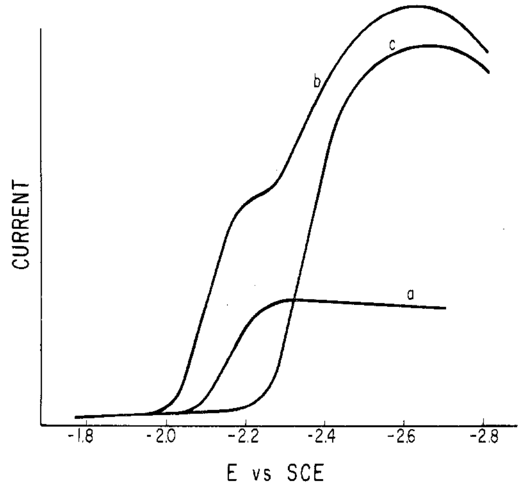
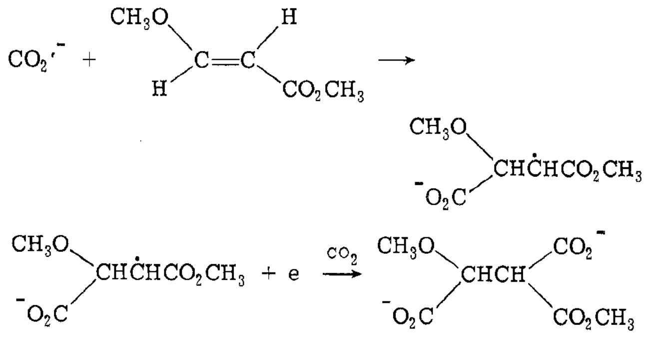


Figure 1. Polarogram of (a) methyl acrylate in acetonitrile saturated with nitrogen and containing 0.1 *M* tetraethylammonium tosylate, (b) methyl acrylate as above, replacing nitrogen by a 1% carbon dioxide–nitrogen mixture, and (c) 1% carbon dioxide–nitrogen mixture only.

consistent with generation of the olefin anion radical and its reaction with carbon dioxide followed by subsequent reduction and further carboxylation.

However, as the reduction potential of the olefin approaches that of carbon dioxide ($E_{1/2}$ = −2.3 V), it becomes less clear whether reduced carbon dioxide (*i.e.*, $CO_2\cdot^-$) or the anion radical of the olefin is the primary electrode product which participates in the subsequent chemical reactions (cie in Table II). In the most extreme case, methyl *trans*-β-methoxyacrylate is reduced *ca.* 0.5 V more negative than carbon dioxide and yet undergoes carboxylation. Thus, an alternate pathway exists for the electrocarboxylation of these olefins. The electrocarboxylation (low yield) of

$$CO_2 + e \longrightarrow CO_2\cdot^-$$



nonelectroactive olefins (norbornadiene and 3,4-dihydropyran) has been reported by us previously.[1] The anion radical of carbon dioxide must unequivocally be involved with these substrates. In addition, certain unsaturated hydrocarbons have been electrocarboxylated: butadiene ($E_{1/2}$ = −2.6 V),[6,7] styrene ($E_{1/2}$ = −2.45 V),[6b,7] naphthalene ($E_{1/2}$ = −2.53 V),[3b,6b,7] and phenanthrene ($E_{1/2}$ = −2.47 V).[3b,7] These substances reduce less readily than carbon dioxide and, thus, the participation of $CO_2\cdot^-$ must be considered in these cases. In this connection, Norman, *et al.*,[8] has shown that $CO_2\cdot^-$ and $\cdot CO_2H$ generated by hydrogen abstraction from HCO_2^- and HCO_2H, respectively, undergo typical radical addition reactions.

Bulk Electrolyses. Partially Aqueous. Several attempts were made to moderate the extent of electrocarboxylation to give monocarboxylated products by replacing the anhydrous solvent–electrolyte mixture with a carbon dioxide saturated solution of aqueous tetraethylammonium bicarbonate. This system would have the advantage of providing a material (*i.e.*, H_2O) which could be sacrificially consumed at the anode to form noninterfering products (*i.e.*, O_2) and, thus, allow a simple undivided cell to be used. However, no carbon dioxide was incorporated under fully aqueous conditions and products typical of electrohydrodimerization were obtained, *i.e.*,[2b]

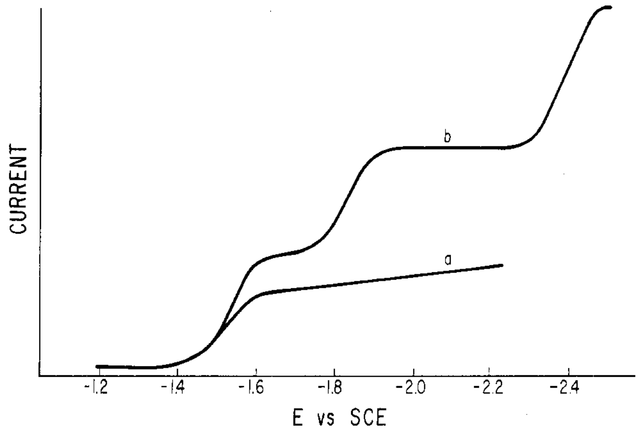


Figure 2. Polarogram of (a) dimethyl maleate in acetonitrile containing 0.1 *M* tetraethylammonium tosylate saturated with nitrogen and (b) replacing nitrogen with 1% carbon dioxide–nitrogen mixture.

$$\text{cathode: } 2CH_2{=}CHX + 2e + 2H_2O \longrightarrow X(CH_2)_4X + 2OH^-$$

$$\text{anode: } H_2O - 2e \longrightarrow {}^1/_2O_2 + 2H^+$$

$$\text{overall cell: } 2CH_2{=}CHX + H_2O \longrightarrow X(CH_2)_4X + {}^1/_2O_2\uparrow$$

$$X = CN, CO_2R$$

The desired reaction was realized by adding water at low levels (2.8 *M*) to an aprotic solvent, proceeding as follows.

$$\text{cathode: } CH_2{=}CHCN + 2e + CO_2 + H_2O \longrightarrow CNCH_2CH_2CO_2^- + OH^-$$

$$\text{anode: } H_2O - 2e \longrightarrow {}^1/_2O_2 + 2H^+$$

$$\text{overall cell: } CH_2{=}CHCN + CO_2 + \underset{(2.8\ M)}{H_2O} \xrightarrow{\text{propionitrile}} CNCH_2CH_2CO_2H + {}^1/_2O_2\uparrow$$

$$ce = 50\%$$

Because a weak acid (CO_2–H_2O) is being converted to a stronger acid ($CNCH_2CH_2CO_2H$), hydrogen evolution was observed soon after the electrolysis was begun. In order to avoid extensive hydrogen evolution a system was designed (Figure 3) which would provide both for the continuous removal of 3-cyanopropionic acid and reequilibration of the circulating propionitrile with water so as to maintain the desired level of water.[9] Extraction of the electrolyte from propionitrile by water was avoided by the use of the water-insoluble salt, tetrabutylammonium tetrafluoroborate. The acid was isolated by extraction of the aqueous solution after acidification.

In conclusion, carbon dioxide effectively traps anionic electrode intermediates generated by reduction of mono- and diactivated olefins in both anhydrous and partially aqueous environments. Comparison of the polarographic behavior of the olefin in the presence and absence of dissolved carbon dioxide can be used as one criterion of reac-

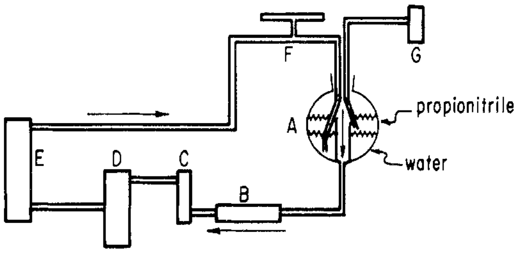


Figure 3. Electrolysis apparatus for monocarboxylation: A, extraction vessel; B, circulating pump; C, flowmeter; D, cooling coil; E, undivided cell containing cadmium cathode and lead oxide anode; F, acrylonitrile inlet; G, carbon dioxide inlet.

tivity provided that there is not interference from the reduction wave of carbon dioxide. The following summarizes the types of reactivity observed.

(1) Activated olefins exhibiting a single two-electron wave in the presence of carbon dioxide are converted under anhydrous conditions to substituted succinic acids provided that the concentration of unreduced olefin is low relative to that of dissolved carbon dioxide.

(2) Activated olefins exhibiting two distinct one-electron waves in the presence of carbon dioxide are converted under anhydrous conditions to α,α' disubstituted succinic acids provided that the potential is maintained on the plateau of the second wave.

(3) Olefins reducing at potentials near or more negative than that of carbon dioxide are also converted to substituted succinic acids under anhydrous conditions. The pathway by which products are obtained is not clear.

(4) Water can be used to moderate the extent of carboxylation. Under partially aqueous conditions β-substituted propionic acids are obtained.

Experimental Section

Equipment. The potentiostat was a Wenking Model 66TS10; the constant-current power supply was a Sorensen DCR300-2.5. Total current passed was measured using a Lectrocount, Royson ENGINEERING Co., Hatboro, Pa. Polarograms were obtained with a Sargent Model XXI polarograph. Nmr spectra were determined at 60 MHz with a Varian A-56/60 or T-60 spectrometer. Analytical glc determinations were made using a Varian Series 1200 gas chromatograph; preparative glc separations employed the Model 770 F & M instrument. The electrolysis cell for the anhydrous electrocarboxylations was a two-compartment H cell, similar to that described previously.[2a] The cell compartments were separated by a 30-mm diameter medium porosity frit. The mercury cathode had an area of 50 cm^2 and the platinum anode an area of 6 cm^2. A combination of mechanical stirring and gas dispersion was employed to mix the catholyte solution. A ground-glass multiport head was fitted to the top of the cathode compartment with provisions for olefin addition, carbon dioxide addition, and system venting through a drying tube. A reference sce was positioned at the mercury surface and as close to the frit as possible.

Reagents and Starting Materials—Reagent-grade acetonitrile was obtained from Matheson Coleman and Bell. The water analysis indicated less than 80 ppm water and, thus, the solvent was used without further purification or drying. Propionitrile was used as commercially obtained. Methyl acrylate, methyl methacrylate, methyl crotonate, dimethyl maleate, acrylonitrile, methacrylonitrile, and methyl vinyl ketone were obtained from commercial sources. They were redistilled and stored with a trace of dissolved hydroquinone prior to being electrolyzed. The preparation of methyl *trans*-β-methoxyacrylate has been described previously.[10] Tetraethylammonium *p*-toluenesulfonate (Aldrich) was recrystallized several times from acetone and dried in a vacuum oven. Tetrabutylammonium tetrafluoroborate was prepared by mixing equimolar amounts of tetrabutylammonium bromide (Eastman) and sodium tetrafluoroborate (Ozark-Mahoning) in water. The solid tetrabutylammonium tetrafluoroborate was isolated by filtration and recrystallized several times from methanol. The carbon dioxide was "bone dry" grade.

Reference Compounds. These were prepared as follows: trimethyl 1,1,2-ethanetricarboxylate by the reaction of sodium dimethyl malonate and methyl bromoacetate;[11] tetramethyl 1,1,2,2-ethanetetracarboxylate by the oxidative coupling of sodium dimethyl malonate;[12] dimethyl 2-cyanosuccinate by the reaction of sodium methyl cyanoacetate and methyl chloroacetate;[13] dimethyl 2-acetylsuccinate by the reaction of sodium methyl acetoacetate and methyl chloroacetate;[14] sodium 3-cyanopropionate by ring opening propiolactone with sodium cyanide.[15] Methyl levulinate was obtained from commercial sources. The spectra and physical properties of all compounds were consistent with those reported.

General Electrolysis Procedure. Dicarboxylation. Depending upon the reduction potential of the activated olefin relative to carbon dioxide, the electrolyses in anhydrous solvents were carried out under conditions of either constant current or constant cathode potential (cie and cpe in Table II). 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 for a sacrificial anode reaction (*i.e.*, $Cl^- - e \rightarrow \frac{1}{2}Cl_2$). The cell and its contents were cooled to 0° with an external ice bath while the solution was saturated for 15 min with 100% CO$_2$. For cpe experiments, the potentiostat was set at the desired cathode voltage and 0.06 mol of activated olefin in 10 ml of acetonitrile was added gradually to the catholyte from a

Table III
Analytical and Nmr Spectral Data

Registry no.	Compd	Bp, °C (mm)	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Spectral data, δ ppm[a]
39994-40-6	Trimethyl 1,2,2-propanetricarboxylate	85 (0.4)	49.5	6.48	49.75	6.64	3.78 (6 H, s, OCH$_3$), 3.71 (3 H, s, OCH$_3$), 2.97 (2 H, s, CH$_2$), 1.56 (3 H, s, CH$_3$)
52003-37-9	Trimethyl 1,1,2-propanetricarboxylate	84 (0.2)	49.5	6.48	50.07	6.72	3.80 (1 H, d, CHX$_2$), 3.78 (6 H, d, OCH$_3$),[b] 3.7 (3 H, s, OCH$_3$), 3.2 (1 H, m, CHX), 1.2 (3 H, d, CH$_3$)
52003-38-0	Trimethyl 2-methoxy-1,1,2-ethanetricarboxylate	87 (1)	46.15	5.98	46.25	6.03	4.92 (1 H, d, CHX), 3.81 (1 H, d, CHX$_2$), 3.78 (6 H, s, OCH$_3$), 3.7 (3 H, s, OCH$_3$), 3.55 (3 H, s, OCH$_3$)
52003-39-1	Dimethyl 2-methyl-2-cyanosuccinate	95 (0.2)	51.89	5.95	50.89	5.70[d]	3.85 (3 H, s, OCH$_3$), 3.75 (3 H, s, OCH$_3$), 2.85 (2 H, q, CH$_2$),[c] 1.63 (3 H, s, CH$_3$)

[a] Solvent CDCl$_3$ with TMS internal standard; X = CO$_2$CH$_3$. [b] Nonequivalent CO$_2$CH$_3$ due to adjacent asymmetric carbon. Separation *ca.* 1 Hz. [c] Nonequivalent CH$_2$ due to adjacent asymmetric carbon. [d] Calcd: N, 7.57. Found: N, 7.82.

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.

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

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Electrocarboxylation. II.[1] Electrocarboxylative Dimerization and Cyclization

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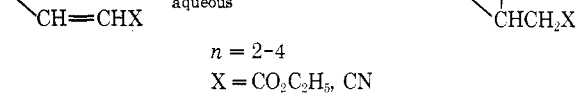
The competitive reactions of electrochemically generated anion radicals of activated olefins with carbon dioxide and unreduced activated olefins have been studied. Dimethyl maleate and carbon dioxide are converted to 1,1,2,3,4,4-hexasubstituted butane derivatives *via* dimerization of electrochemically 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).



$$(CH_2)_n\begin{cases}CH{=}CHX\\CH{=}CHX\end{cases} \xrightarrow[\text{aqueous}]{+e} X(CH_2)_{n+4}X + (CH_2)_n\begin{cases}CHCH_2X\\CHCH_2X\end{cases} \quad (1)$$

$n = 2\text{–}4$

$X = CO_2C_2H_5$, CN