Organic Chemistry

Electrocarboxylation of 1,4-dibromobut-2-ene in a CO_2—DMF liquid mixture

V. A. Grinberg,[a] T. A. Koch,[b] V. M. Mazin,[a] E. I. Mysov,[a] and S. R. Sterlin[a]*

[a]A. N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117071 Moscow, Russian Federation. Fax: 007 (095) 952 0846

[b]Central Research and Development E. I. Du Pont de Nemours and Company, Inc., Experimental Station, P.O. Box 80262, Wilmington, DE 19880-0262, USA. Fax: 001 (302) 695 9084

The possibility of synthesizing dihydromuconic acid by cathodic carboxylation of 1,4-dibromobut-2-ene in the liquid CO_2—aprotic solvent system was investigated. The low yield of dihydromuconic acid in this reaction was explained by the competing reductive debromodimerization and oligomerization of 1,4-dibromobut-2-ene, which lead to the predominant formation of 1,8-dibromo-2,6-octadiene and polymeric products.

Key words: 1,4-dibromobut-2-ene, electrochemical carboxylation.

Electrocarboxylation of 1,3-butadiene aimed at synthesizing adipic acid has been one of the most topical problems in synthetic electroorganic chemistry for more than 30 years.[1—8] The mechanism of this reaction, which yields dihydromuconic acid, a precursor of adipic acid, is still debated.

In the opinion of some researchers, this reaction involves the addition of radical anions derived from carbon dioxide to butadiene;[7] other researchers believe that butadiene is initially reduced to give allyl anions, which react with carbon dioxide as nucleophiles.[9] However, the fact that in both cases, the arising intermediate species react with each other at the surface of the cathode can be considered to be well established.[7] The composition and the yields of the products of electrocarboxylation of butadiene depend markedly on the nature of the electrode material,[6] which suggests that this reaction is electrocatalytic.

Study of the electrocarboxylation of butadiene in a liquid CO_2—DMF mixture containing 0.1 *M* Bu_4NBr as the supporting electrolyte in a diaphragmless electrochemical cell equipped with a lead cathode at a potential of −2.25 V and at various concentrations of CO_2 (the corresponding polarization curves are presented in Fig. 1) has shown that, in addition to products normal for this reaction, *viz.*, dihydromuconic ($HOOCCH_2CH{=}CHCH_2COOH$, **1**) and oxalic acids (**2**), the reaction yields 5-bromopent-3-enoic acid (**3**). GC/MS analysis has shown that the proportion of acid **1** in the reaction products increases in parallel with the concentration of CO_2.

The fact that the bromo-containing acid **3** is found among the reaction products is due to the anodic generation of bromine; two pathways to compound **3** can be proposed:

(a) conjugated radical bromocarboxylation of butadiene

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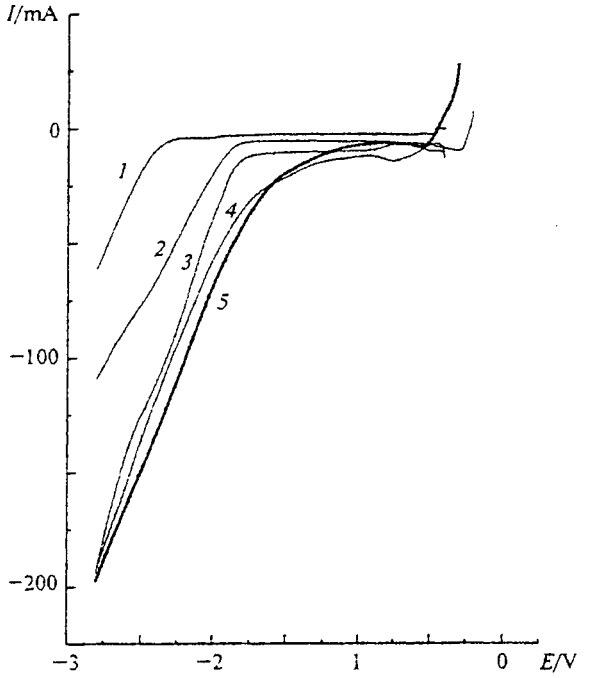

Fig. 1. Voltammograms recorded on a lead electrode (10 cm^2) in DMF with 0.1 *M* Bu_4NBF_4 (*1*), in the presence of 1,3-butadiene (18.5 mmol L^{-1}) (*2*) and its mixture with CO_2 at a pressure of 0.8 (*3*) or 4.0 MPa (*4*), and after the electrolysis performed under the conditions of entry *1* (*5*) (see Experimental). Scan rate is 10 mV s^{-1}.

$$CO_2 + e^- \longrightarrow CO_2^{\cdot -}(ads),^*$$

$$CO_2^{\cdot -}(ads) + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow$$

$$\longrightarrow {}^-O_2CCH_2CH{=}CHCH_2^{\cdot} \xrightarrow[-Br^{\cdot}]{Br_2}$$

$$\longrightarrow {}^-O_2C{-}CH_2CH{=}CHCH_2Br;$$

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(b) cathodic carboxylation of 1,4-dibromobut-2-ene (**4**) resulting from anodic bromination of butadiene.

The second pathway is of special interest, because it can lead not only to 5-bromopent-3-enoic acid **3** but also to dihydromuconic acid **1**.

This work was undertaken in order to study the cathodic carboxylation of 1,4-dibromobut-2-ene.

Results and Discussion

Electroreduction of 1,4-dibromobut-2-ene at various electrodes in methanol and DMF. Figures 2—4 present typical polarization curves for electroreduction of dibromobutene **4** obtained for electrodes made of various materials and in solvents of various natures. The polarization curves normally exhibit an irreversible wave with a typical drop of the current in the region of its limiting values. Depending on the nature of the material

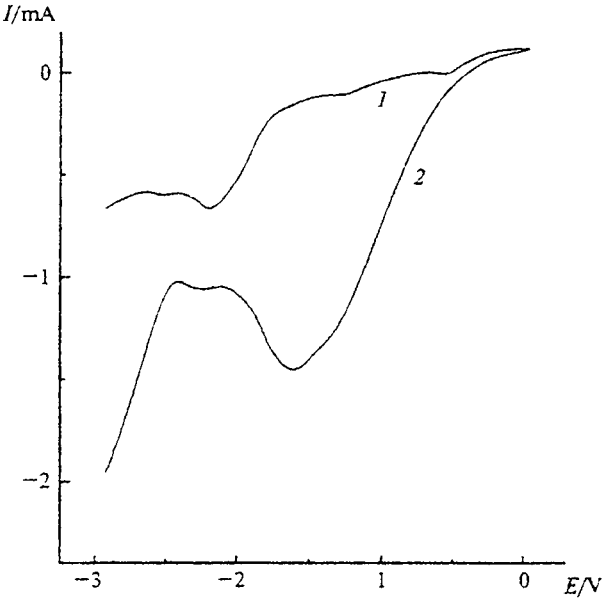

Fig. 2. Voltammograms recorded on a lead electrode (0.03 cm^2) in DMF with 0.1 *M* Bu_4NBF_4 (*1*) and in the presence of 1,4-dibromobut-2-ene (0.1 mmol L^{-1}) (*2*). Scan rate is 300 mV s^{-1}.

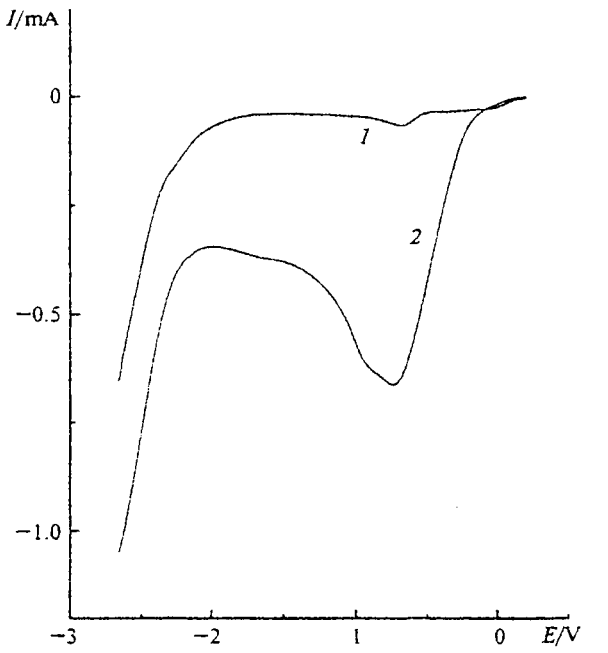

Fig. 3. Voltammograms recorded on a stainless-steel electrode (0.2 cm^2) in DMF with 0.1 *M* Bu_4NBF_4 (*1*) and in the presence of 1,4-dibromobut-2-ene ($2 \cdot 10^{-2}$ mmol L^{-1}) (*2*). Scan rate is 100 mV s^{-1}.

* The formation of oxalic acid in the cathodic reduction of CO_2 has been considered previously.[10,11]

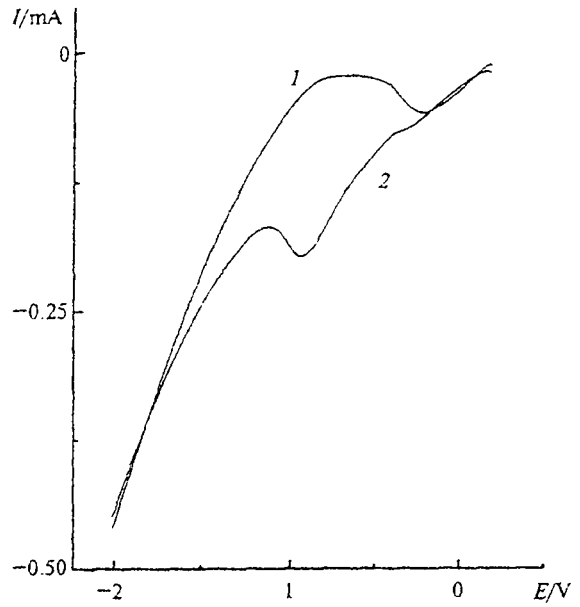

Fig. 4. Voltammograms recorded on a copper electrode (0.03 cm^2) in MeOH with 0.1 *M* Bu_4NBF_4 (*1*) and in the presence of 1,4-dibromobut-2-ene ($2 \cdot 10^{-2}$ mmol L^{-1}) (*2*). Scan rate is 100 mV s^{-1}.

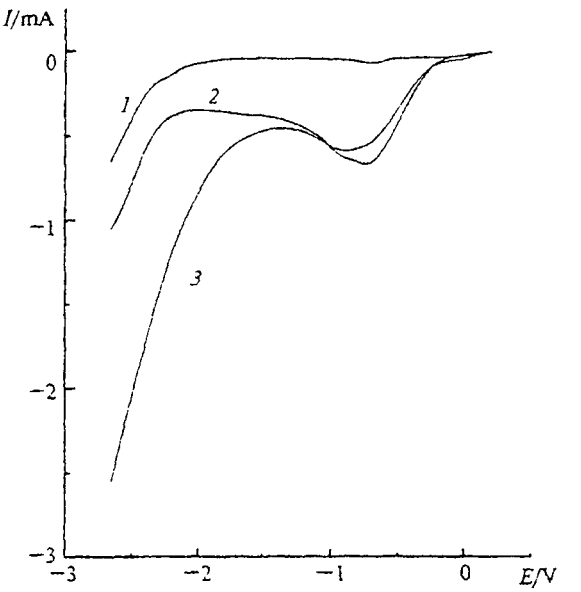

Fig. 5. Voltammograms recorded on a stainless-steel electrode (0.2 cm^2) in DMF with 0.1 *M* Bu_4NBF_4 (*1*) and in the presence of 1,4-dibromobut-2-ene ($2 \cdot 10^{-2}$ mmol L^{-1}) (*2*) and in the same solution saturated with CO_2 under atmospheric pressure (*3*). Scan rate is 100 mV s^{-1}.

of the electrode and on the solvent, this wave is observed over a broad range of potentials (from 0.25 to −2.5 V). Unlike butadiene, which is reduced at large cathodic potentials, dibromide **4** is reduced at relatively small cathodic polarizations. This is caused by the fact that molecule **4** is more electrophilic than butadiene owing to the presence of Br atoms. These studies showed that the reduction wave of compound **4** has a diffusion nature (the dependence of the maximum current on the square root of the rate of the potential sweep is linear and passes through the origin of the coordinates) and corresponds to the transfer of one electron (the current in the maximum calculated from the Randles—Ševčik[12] equation is in good agreement with the experimental value obtained assuming the transfer of one electron). This is also confirmed by the results of MS analysis of the electrolysis products. Electroreduction of dibromobutene **4** in DMF at copper or stainless-steel electrodes at −1.5 V (entry *2*) afforded 1,8-dibromo-2,6-octadiene (**5**) as the major product; some quantity of polymeric products was also detected. It should be noted that preparative electroreduction of dibromide **4** in DMF at a lead electrode results in intense destruction of the electrode. This is apparently due to the formation of organolead compounds during the interaction of electrochemically generated allyl-type radicals, *viz.*, bromobutenyl, 8-bromooctadienyl, *etc.*, with the material of the electrode. For example, it is known that in the electroreduction of ethyl bromide on lead in propylene carbonate, tetraethyllead is formed.[13]

When compound **4** is reduced at copper and lead electrodes in methanol, these electrodes are also destroyed; however a copper cathode is dissolved to a lesser extent than a lead cathode.

Figure 5 shows the polarization curve for the electroreduction of a mixture of dibromide **4** and CO_2 at a stainless-steel electrode in a 0.1 *M* solution of Bu_4NBF_4 in DMF. It can be seen from this figure that electroreduction of CO_2 occurs at potentials more negative than −1.5 V, whereas compound **4** is reduced at less negative potentials.

This made it possible to accomplish potentiostatic electrolysis of a mixture of dibromide **4** and CO_2 at −1.5 V at a stainless-steel electrode in DMF. However, we found that the electrolysis at potentials corresponding to the limiting current of the electroreduction of compound **4** does not yield any products of the carboxylation of intermediate species. According to GC/MS analysis, the main products of this reaction were the same as in the electrolysis of compound **4** without CO_2, namely, compound **5** and the polymer. Thus, the only route of transformation of compound **4** under these conditions is reductive debromination to give products of dimerization and polycondensation.

Study of the electrocarboxylation of 1,4-dibromobut-2-ene in the potential range of the electroreduction of CO_2. Potentiostatic electrolysis of a mixture of 1,4-dibromobut-2-ene and CO_2 at the potentials of reduction of dibromide **4** gave no electrocarboxylation products. Therefore, we studied the possibility of accomplishing

electrocarboxylation of compound **4** during the potentiostatic electrolysis of the same mixture carried out at the reduction potentials of CO_2. Under these conditions, radical anions produced from carbon dioxide are formed in parallel with the bromobutenyl radicals produced from compound **4**. Depending on the nature of the electrode material, the cathodic potential, and the concentration of the starting compounds, the partial rates of the generation of radical anions from dibromide **4** and CO_2 can be markedly dissimilar, which should have an effect on the yields of target products.

In the preparative electrolysis of a mixture of 1,4-dibromobut-2-ene and CO_2, we had to take into account the possibility of the formation of Br_2 through anodic oxidation of the bromide ions arising during the cathodic reduction of compound **4**. It is clear that the presence of Br_2 in the reaction medium would markedly decrease the current yields of the products obtained in the electroreduction of dibromide **4** and CO_2 owing to the competing reduction of bromine. Therefore, to bind the bromine, 1,3-butadiene was added to the reaction mixture in a quantity equimolar to that of compound **4**. It should be emphasized that in the case of potentiostatic electrolysis, the effect of free bromine on the electrocarboxylation of dibromide **4** in the potential range of reduction of CO_2 is not very pronounced, because the partial current of the reduction of bromine (at the limiting current) accounts for only a small fraction of the currents spent for the reduction of compound **4** and CO_2. This is clearly illustrated by the experiments carried out under potentiostatic conditions with and without 1,3-butadiene (the current yields of acid **1** in entries *3* and *5* are close).

Preparative electrolysis of a mixture of 1,3-butadiene, 1,4-dibromobut-2-ene, and CO_2 in DMF carried out at a stainless-steel electrode at −2.25 V (entry *3*) gave dihydromuconic acid,* along with the products resulting from dimerization of the $BrCH_2CH{=}CHCH_2^{\cdot}$ radicals (1,8-dibromo-2,6-octadiene, **5**) and of the radical anions derived from carbon dioxide (oxalic acid).[1]

It should be noted that the preparative electrolysis carried out under the same conditions but with a copper electrode instead of the stainless-steel cathode (entry *4*) did not lead to dihydromuconic acid. Among the electrolysis products, we detected oxalic acid and a large quantity of the polymer formed apparently by the polymerization of the intermediate species arising in the electroreduction of the initial 1,4-dibromobut-2-ene.

To make sure that 1,3-butadiene does not participate in the formation of dihydromuconic acid, we carried out the electrocarboxylation at a stainless-steel cathode in the absence of 1,3-butadiene (entry *5*). It was found that in this case, as in the presence of 1,3-butadiene, the electrode process afforded oxalic and dihydromuconic acids as the major products; a substantial amount of polymers was also detected.

Thus, we have shown the possibility of accomplishing a new electrochemical reaction, *viz.*, electrocarboxylation of 1,4-dibromobut-2-ene in the liquid CO_2—aprotic solvent system. Dihydromuconic acid is formed apparently by a radical mechanism. The possibility of carrying out electrocarboxylation of 1,4-dibromobut-2-ene depends on the nature of the electrode material, which is probably due to the different electrocatalytic activities of cathodic materials in the reductive debromination of compound **4**.

Experimental

The recording of polarization curves and the preparative electrolyses at high pressures were carried out in a diaphragmless electrochemical cell, which was an autoclave designed to operate at a pressure of up to 150 atm. Three conductors serving to connect the working, auxiliary, and reference electrodes were built into the autoclave cover through Teflon insulators.

The preparative electrolyses under atmospheric pressure were carried out in a glass cell equipped with a water jacket and a reflux condenser; the electrolyte was stirred with a magnetic stirrer.

A PAR 273 computerized system was used to record polarization curves and to conduct the preparative electrolyses.

Methanol for voltammetry and DMF for voltammetry and for preparative electrolyses were purified by standard procedures and then twice distilled. 1,4-Dibromobut-2-ene (*trans*-isomer) was prepared* by a previously reported procedure.[14]

Prior to polarization measurements, the electrodes were subjected to the standard workup, *i.e.*, they were conditioned using a fine abrasive, degreased in hot alcohol, thoroughly washed with distilled water, and dried in a vacuum dessicator.

Prior to the measurements at elevated or atmospheric pressures, the initial electrolyte was thoroughly purged with argon in order to remove traces of oxygen.

The pressure of CO_2 in the working cavity of the electrochemical cell was maintained using a cylinder with liquid carbon dioxide kept at a required temperature. The temperature in the electrochemical cell was maintained by controlling the temperature in the water jacket of the autoclave. The electrolyte solution was saturated with 1,3-butadiene under atmospheric pressure, and the change in the weight was monitored, or a weighed quantity of 1,3-butadiene was introduced into the cell prior to the addition of CO_2 by a procedure described previously.[15]

All the potentials were measured and given *vs.* an Ag-quasi reference electrode;[16] in all cases, electrolysis was carried out at 25 °C.

When the electrolysis was completed, the gaseous products were released through a trap (−78 °C) into a gasometer. The gases and the liquid fraction were analyzed using a VG-7070 E GC/MS spectrometer (ionization energy was 70 eV; OV-101 as the stationary phase; 30 °C (5 °C min^{-1})).

Examples of electrosynthesis. *Entry 1.* A 0.1 *M* solution of Bu_4NBF_4 in DMF (15 mL) containing Bu_4NBr (2 g,

* Other researchers[6] found no products of the electrocarboxylation of butadiene on a stainless-steel electrode. Apparently, the presence of a diaphragm in this case made impossible the formation of dibromide **4** participating in the electroreduction.

* The authors are grateful to V. F. Cherstkov, who provided the sample of 1,4-dibromobut-2-ene.

6.2 mmol) and 1,3-butadiene (1 g, 18.5 mmol) was placed in a diaphragmless high-pressure electrochemical cell, a CO_2 pressure equal to 4 MPa was established, and the mixture was subjected to potentiostatic electrolysis at a lead cathode (12 cm^2) and a platinum anode (10 cm^2) at a cathodic potential of −2.25 V. When 2100 C of charge had been passed through the mixture, the electrolysis was stopped, and the electrolyte was treated with an aqueous solution of K_2CO_3 to pH 9 and concentrated using a rotary evaporator; the solid residue was treated with dilute (1 : 1) HCl or 15% H_2SO_4 and extracted three times with diethyl ether, then the ether was evaporated, and the residue was treated with diazomethane in ether until the evolution of nitrogen completely ceased. The ethereal solution was concentrated and analyzed. Evaporation of the ether gave 0.3 g of organic products.

The following electrolysis products were identified by GC/MS analysis: **dimethyl dihydromuconate, $CH_3OCOCH_2CH{=}CHCH_2COOCH_3$ (1a)**, *m/z* (I_{rel} (%)): 172 $[M]^+$ (3), 141 $[M-CH_3O]^+$ (40), 140 $[C_7H_8O_3]^+$ (30), 113 $[C_6H_9O_2]^+$ (59), 112 $[C_6H_8O_2]^+$ (38), 99 $[C_5H_7O_2]^+$ (32), 81 $[C_5H_5O]^+$ (20), 71 $[C_3H_4O_2]^+$ (100), 59 $[CO_2Me]^+$ (88), 53 $[C_4H_5]^+$ (25), 41 $[C_3H_5]^+$ (38), 39 $[C_3H_3]^+$ (25), 27 $[C_2H_3]^+$ (20), 15 $[CH_3]^+$ (75); **methyl 5-bromopent-3-enoate, $BrCH_2CH{=}CHCH_2COOCH_3$ (3a)**, *m/z* (I_{rel} (%)): 192 $[M]^+$ (23), 113 $[M-Br]^+$ (20), 69 $[C_5H_9]^+$ (20), 55 $[C_4H_7]^+$ (18), 41 $[C_3H_5]^+$ (78), 39 $[C_3H_3]^+$ (100), 27 $[C_2H_3]^+$ (25).

Compound **4**, whose mass spectrum coincides with the reference spectrum (NBS 18560) and dimethyl oxalate (NBS 2866) were also detected among the electrolysis products. The current yield of compound **1** did not exceed 3%.

Entry 2. A 0.1 *M* solution of Bu_4NBF_4 (30 mL) in DMF containing compound **4** (1 g, 4.7 mmol) was placed in a glass diaphragmless electrochemical cell with a stainless-steel cathode (a 10 cm^2 grid) and a platinum anode (10 cm^2), and the mixture was subjected to potentiostatic electrolysis at a cathode potential of −1.5 V. After 500 C of charge had been passed through the mixture, the electrolysis was stopped, the solvent was evaporated *in vacuo*, and the residue (0.5 g) was dissolved in diethyl ether and analyzed by GC/MS. A product was detected, whose mass spectrum corresponded to **1,8-dibromo-2,6-octadiene, $BrCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2Br$ (5)**, *m/z* (I_{rel} (%)): 187 $[M-Br]^+$ (23), 100 $[M-Br-HBr]^+$ (100). According to GLC, the proportion of compound **5** in the reaction products amounted to 68%, which corresponded to a current yield of **5** of 54.5%. In addition, the reaction mixture obtained after the electrolysis contained polymeric products.

Entry 3. A 0.1 *M* solution of Bu_4NBF_4 (20 mL) in DMF containing Bu_4NBr (1.5 g, 4.5 mmol), and compound **4** (0.5 g, 2.4 mmol), which had been saturated with 1,3-butadiene under atmospheric pressure (0.13 g, 2.4 mmol), was placed in a diaphragmless high-pressure electrochemical cell; a CO_2 pressure of 4 MPa was established, and the mixture was subjected to potentiostatic electrolysis at a stainless-steel cathode (10 cm^2) and a platinum anode (10 cm^2) at a cathode potential of −2.25 V. After 1207 C of charge had been passed through the mixture, the electrolysis was stopped, and the electrolyte was worked up as in entry *1*. Evaporation of the ether gave 30 mg of organic products. GC/MS analysis showed the presence of the initial dibromide **4**, dimethyl dihydromuconate **1a** (its mass spectrum is presented in entry *1*), dimethyl oxalate, and compound **5**. The current yield of compound **1** did not exceed 5%.

Entry 4. A 0.1 *M* solution of Bu_4NBF_4 (15 mL) in DMF containing Bu_4NBr (0.5 g, 1.5 mmol), compound **4** (0.5 g, 2.4 mmol), and 1,3-butadiene (0.13 g, 2.4 mmol) was placed in a high-pressure diaphragmless electrochemical cell; a CO_2 pressure of 4 MPa was established, and the mixture was subjected to potentiostatic electrolysis at a copper cathode (10 cm^2) and a platinum anode (10 cm^2); the cathode potential was −3.0 V. After 809 C of charge had been passed through the mixture, the electrolysis was stopped, and the electrolyte was worked up as in entry *1*. Evaporation of the ether gave 50 mg of organic products. GC/MS analysis of the reaction products showed the presence of dimethoxyethane (NBS 877), dimethyl oxalate (NBS 2866), and a large amount of a polymer. No products of the electrocarboxylation of dibromide **4** and 1,3-butadiene were found. Compound **5** also was not detected among the electrolysis products.

Entry 5. A 0.1 *M* solution of Bu_4NBF_4 (20 mL) in DMF containing Bu_4NBr (1.4 g, 4.5 mmol) and compound **4** (0.25 g, 1.2 mmol) was placed in a high-pressure diaphragmless electrochemical cell, a CO_2 pressure of 4 MPa was established, and the mixture was subjected to potentiostatic electrolysis at a stainless-steel cathode (10 cm^2) and a platinum anode (10 cm^2); the cathode potential was −2.25 V. After 1237 C of charge had been passed through the mixture, the electrolysis was stopped, and the electrolyte was worked up as in entry *1*. Evaporation of the ether gave 70 mg of organic products. GC/MS analysis of the mixture detected dimethyl dihydromuconate **1a**, dimethyl oxalate, and a substantial amount of a polymer. The current yield of compound **1** did not exceed 5%.

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