Electrochemical oxidation of malonic esters in acetonitrile in the presence of iodides as mediators

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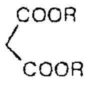
Electrochemical oxidation of malonic esters in acetonitrile in the presence of iodides follows two different pathways depending on the nature of the cation. In the presence of LiI, alkyl 1,1,2,2,3,3-propanetetracarboxylates were obtained in 85—98% yields. In the presence of NaI, KI, or Bu_4NI, the formation of 1,1,2,2-ethanetetracarboxylates and their subsequent dehydrogenation to ethenetetracarboxylates was the main reaction pathway.

Key words: electrochemical oxidation, malonic ester, mediators, esters of polycarboxylic acids.

Electrochemical oxidation of the anions of malonic esters (**1**) results in the formation of dimers (**2**).[1,2] The outcome of indirect electrochemical oxidation of the anions of malonic esters in alcohols depends on the nature of the mediator, the temperature, and the amount of electricity passed. Depending on the conditions, along with dimers **2**, this process yields compounds **3**—**6** in relatively high yields.[3—5]



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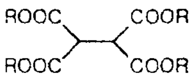

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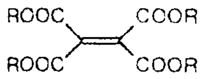

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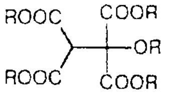

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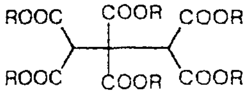

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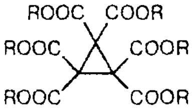

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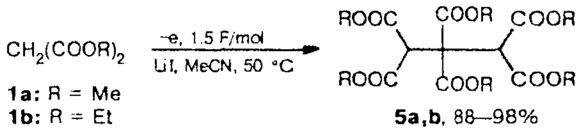
If iodides in alcohols are used as mediators, tetraalkyl ethylenetetracarboxylates (**3**) and alkoxyethanetetracarboxylates (**4**) are formed.[3] The electrooxidation of dialkyl malonates in alcoholic solutions in the presence of bromides as mediators is an efficient method of performing linear or cyclic trimerization of malonic ester to esters **5** and **6**.[4,5]

The electrochemical oxidation of dialkyl malonates in acetonitrile in the presence of mediators has been less studied. Only the formation of dimers **2** in the electrooxidation of malonic esters in acetonitrile in the presence of KI[6] and the linear electrochemical trimerization of malonic ester in acetonitrile in the presence of LiBr[4] have been reported. However, bromides of other alkali metals are poorly soluble in acetonitrile and, therefore, they cannot be used as mediators in this solvent.

In this work, we studied the electrochemical oxidation of dialkyl malonates in acetonitrile in the presence of alkali metal iodides (Table 1).

Electrolysis of dimethyl or diethyl malonate was carried out using direct current in a diaphragmless electrolyzer equipped with a platinum or graphite anode and an iron cathode. The process was continued until dialkyl malonate **1** was converted completely or to a large extent.

The data of Table 1 indicate that when the LiI—MeCN system is used, malonic esters trimerize almost quantitatively at 50 °C after 1.5 F/mol of electricity has been passed.



In the NaI—MeCN system, to achieve complete conversion of malonic esters, a larger amount of electricity is needed. Tetraalkyl ethylenetetracarboxylate **3** is formed as a major reaction product in a yield of more than 80% at the optimum temperature, which is 20 °C. At 50 °C, esters **3** and **5** are obtained in the same system in 49 and 40% yields, respectively.

The electrooxidation of malonic ester in the KI—MeCN and Bu_4NI—MeCN systems occurs similarly to that in the NaI—MeCN system; however, it is less efficient.

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Table 1. Electrochemical oxidation of $CH_2(COOR)_2$ **1a,b** in MeCN in the presence of salts of hydroiodic acid[a]

Entry	R	Electrolyte	T/°C	Q,[b] /F mol^{-1}	β[b] (%)	Substance (current) yield (%)[c]		
						2	**3**	**5**
1	Me	LiI	50	1.4	93	—	—	93(89)
2	Me	LiI	50	1.5	100	—	—	98(87)
3	Me	LiI	20	1.9	100	—	15	85(60)
4	Et	LiI	50	1.5	100	—	—	88(78)
5	Me	NaI	50	2.1	100	10	49	40
6	Me	NaI	20	2.3	100	—	85 (74)	15
7	Et	NaI	20	2.3	100	—	82 (71)	18
8[d]	Me	KI	20	2.3	91	16	67	8
9	Me	Bu_4NI	20	2.3	83	23	50	9

[a] 16 mmol of **1** and 8 mmol of an electrolyte in 20 mL of MeCN.

[b] Q is the amount of electricity; β is the degree of conversion.

[c] The yield is based on the compound **1** taken and found by GLC and ^1H NMR spectroscopy.

[d] The current density was 110 mA cm^{-2}; in the rest of the entries it was 220 mA cm^{-2}.

The effect of the nature of the cation in the mediator on the composition of the electrolysis products has also been observed previously in a study of the electrooxidation of diethyl malonate in alcohols;[3] however, this effect was far less pronounced than that observed in the case of acetonitrile.

The results of the electrolysis in acetonitrile make it possible to divide the mediators studied into two groups. One group includes lithium iodide, and the other group comprises the rest of the iodides studied. When lithium iodide was used as the mediator at 50 °C, only one reaction product, linear trimer **5**, was identified in the reaction mixture irrespective of the degree of conversion of dialkyl malonate **1**.

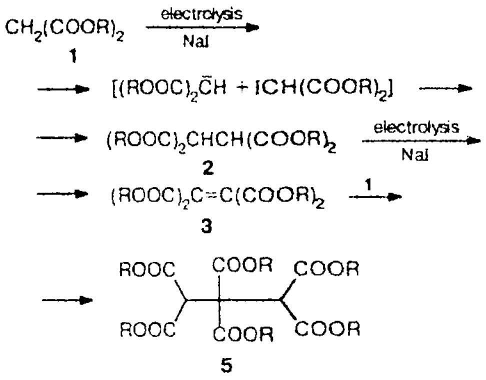
In the presence of NaI, KI, or Bu_4NI, substantial amounts of dimer **2** and dehydrodimer **3** were detected in the reaction mixture at incomplete conversion of compound **1**. Evidently, when electrooxidation of **1** is conducted in acetonitrile in the presence of NaI, KI, or Bu_4NI, the linear trimer **5** is formed by a mechanism similar to that by which compound **5** is formed in the electrooxidation of **1** in the presence of NaI, KI, or Bu_4NI in alcohols,[3] namely *via* the formation of dimer **2** and its dehydrogenation to give **3**. The subsequent addition of dialkyl malonate **1** to product **3** catalyzed by an electrically generated base yields linear trimer **5**.

This mechanism (Scheme 1) is in good agreement with the variation of the composition of the reaction mixture during the electrooxidation of **1a** in acetonitrile in the presence of NaI and KI at 50 °C (Fig. 1, *a*, *b*).

When LiI is used as the mediator, electrooxidation of the diethyl malonate **1** in acetonitrile follows a different mechanism, because it involves no intermediate formation of dimer **2** and dehydrodimer **3** (Fig. 1, *c*).

The strong effect of Li^+ cations on the mechanism of electrooxidation of **1** is most likely due to the fact that Li^+ cations in acetonitrile are able to form "tighter" ion pairs with the diethyl malonate anion than other alkali metal cations.[7] This fact substantially retards nucleophilic substitution yielding dimer **2**, and directs the process along the pathway involving the intermediate formation of dialkyl diiodomalonate (Scheme 2):

Scheme 1



Scheme 2

$$(ROOC)_2\overset{\ominus}{C}H\overset{\oplus}{Li} + CHI(COOR)_2 \longrightarrow (ROOC)_2\overset{\ominus}{C}I\overset{\oplus}{Li} + CH_2(COOR)_2,$$

$$(ROOC)_2\overset{\ominus}{C}I\overset{\oplus}{Li} + I_2 \longrightarrow (ROOC)_2CI_2 + LiI,$$

$$(ROOC)_2CI_2 + 2\,(ROOC)_2\overset{\ominus}{C}I\overset{\oplus}{Li} \longrightarrow \mathbf{5} + 2\,LiI,$$

The dynamics of the conversion of ester **1a** and the accumulation of trimer **5a** are consistent with the mechanism shown in Scheme 2 (Fig. 1, *c*). It should be noted

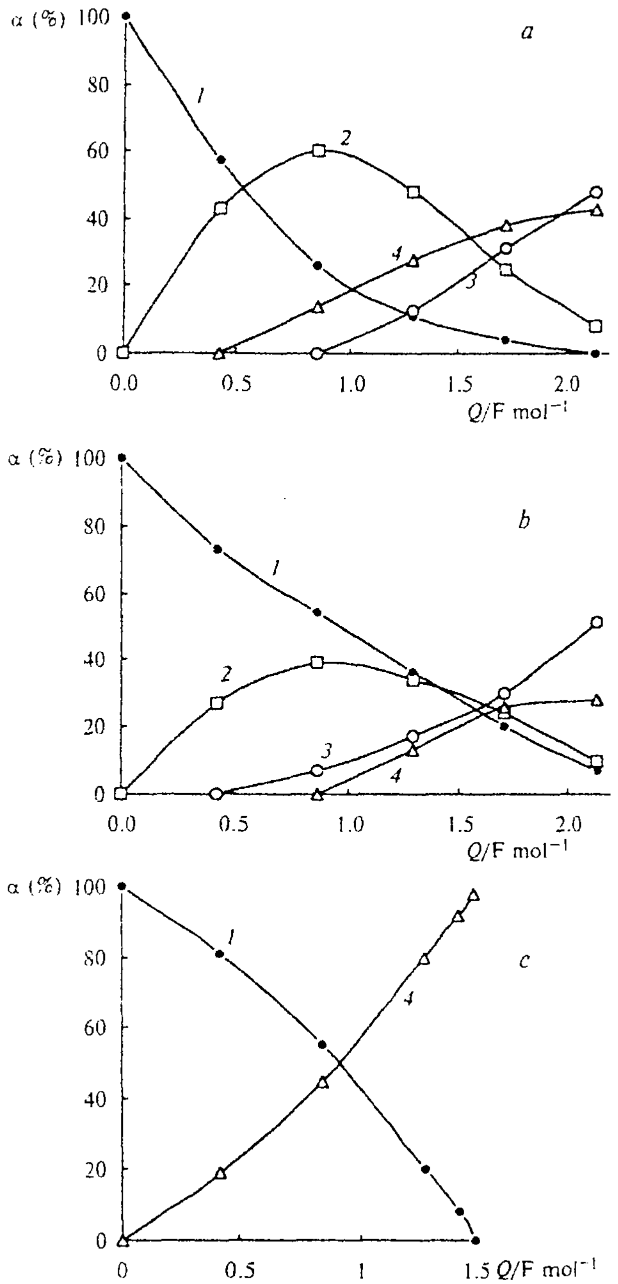


Fig. 1. Variation of the composition of the reaction mixture (α) during the electrolysis of $CH_2(COOMe)_2$ **1a** in MeCN in the presence of salts of hydroiodic acid at 50 °C: NaI (*a*), KI (*b*), LiI (*c*); **1a** (*1*), **2a** (*2*), **3a** (*3*), **5a** (*4*). Q is the amount of electricity.

that the electrolysis carried out in alcohols in the presence of LiI at 50 °C also gave considerable amounts of the trimer. The curve for the accumulation of trimer **5** in MeOH (Fig. 2) starts earlier and during the whole process lies markedly higher than that for the accumulation of dehydrodimer **3**. This makes it possible to assume that electrooxidation of **1** in MeOH in the presence of LiI follows a mixed mechanism.

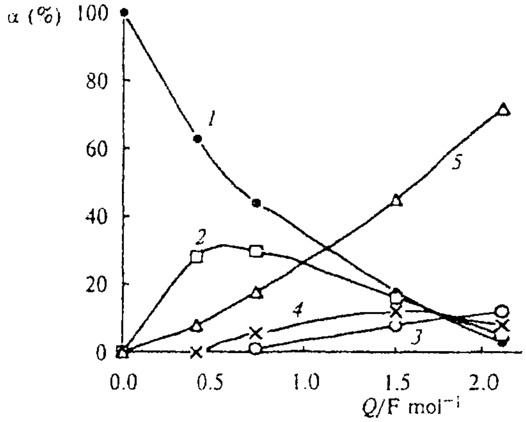


Fig. 2. Variation of the composition of the reaction mixture (α) during the electrolysis of $CH_2(COOMe)_2$ **1a** in MeOH in the presence of LiI at 50 °C: **1a** (*1*), **2a** (*2*), **3a** (*3*), **4a** (*4*), **5a** (*5*).

The electrolysis of dialkyl malonate in alcohols in the presence of NaI at 0 to −20 °C occurs as selective oxidation of compound **1** to dimer **2** and only when a substantial amount of dimer **2** has been accumulated in the mixture does it start to be converted selectively to dehydrodimer **3**.[3] This enabled the preparation of **3** at low temperatures (0 to −20°C) directly from **1** in a 68—78% substance yield and 65—74% current yield.[3]

When electrolysis of **1** is carried out in acetonitrile in the presence of NaI, a similar process can be accomplished even at 20 °C. Dehydrodimer **3** was prepared from **1** in a substance yield of 85% and a current yield of 74% (entry 6, Table 1).

Experimental

^1H and ^{13}C NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (300 MHz) spectrometers; the chemical shifts are presented in the δ scale using tetramethylsilane as the internal standard.

GLC analysis was carried out on an LKhM-8D chromatograph with a flame ionization detector using nitrogen at a velocity of 30 mL min⁻¹ as the carrier gas and a 2500×3 mm stainless-steel column with 5% SE-Superphase on Inerton Super (0.16—0.20 mm).

General procedure. Ester **1** (16 mmol), an electrolyte (mediator) (8 mmol), and 20 mL of a solvent were placed in a diaphragmless electrolyzer with external cooling equipped with a Fe cathode, a Pt anode (the distance between the electrodes was ~5 mm), a magnetic stirrer, a thermometer, and a reflux condenser. The electrolysis was carried out by direct current (at a current density of 220 mA cm^{-2}); the amounts of electricity passed through the cell are listed in Table 1. The reaction mixture was concentrated, and the residue was washed with 20 mL of water and extracted with 50 mL of chloroform. The organic layer was separated, dried with Na_2SO_4, concentrated, and analyzed by GLC and ^{1}H NMR spectroscopy using 1,4-dichlorobenzene as the internal standard.

To construct the curves for the accumulation of electrolysis products (see Figs. 1 and 2), small portions of the reaction mixture were withdrawn at regular intervals during the electrolysis and analyzed by GLC and ^{1}H NMR spectroscopy.

Tetramethyl 1,1,2,2-ethanetetracarboxylate 2a,[2] m.p. 136—137 °C. ^{1}H NMR, δ: 3.76 (s, 12 H, CH_3O), 4.14 (s, 2 H, CH). ^{13}C NMR, δ: 51.1 (d, CH), 52.9 (q, CH_3O), 167.3 (s, C=O).

Tetramethyl ethenetetracarboxylate 3a,[3] m.p. 119—120 °C. ^{1}H NMR, δ: 3.85 (s, 12 H, CH_3O). ^{13}C NMR, δ: 53.2 (q, CH_3O), 135.2 (s, C=C), 162.5 (s, C=O).

Tetraethyl ethylenetetracarboxylate 3b,[3] m.p. 55—56 °C. ^{1}H NMR, δ: 1.35 (t, 12 H, CH_3), 4.29 (q, 8 H, CH_2O). ^{13}C NMR, δ: 13.5 (q, CH_3), 62.1 (t, CH_2O), 135.3 (s, C=C), 162.2 (s, C=O).

Tetramethyl methoxyethane-1,1,2,2-tetracarboxylate 4a,[3] m.p. 54—56 °C (ether—pentane). ^{1}H NMR, δ: 3.54 (s, 3 H, CH_3O), 3.74 and 3.84 (both s, 12 H, CO_2CH_3), 4.23 (s, 1 H, CH). ^{13}C NMR, δ: 52.1, 52.3, and 55.0 (all q, CH_3O), 52.7 (d, CH), 83.9 (s, $\underline{C}$—OMe), 165.4 and 166.9 (both s, C=O).

Hexamethyl propane-1,1,2,2,3,3-hexanecarboxylate 5a,[4] m.p. 136—137 °C. ^{1}H NMR, δ: 3.76 (s, 12 H, CH_3O), 3.79 (s, 6 H, CH_3O), 4.27 (s, 2 H, CH). ^{13}C NMR, δ: 52.6 and 53.0 (both q, CH_3O), 54.1 (d, CH), 58.9 (s, C), 167.3 and 167.9 (both s, C=O).

Hexaethyl propane-1,1,2,2,3,3-hexanecarboxylate 5b,[4] b.p. 184—186 °C (0.25 mm), m.p. 40—42 °C (ether—pentane). ^{1}H NMR, δ: 1.26 and 1.28 (both t, 18 H, CH_3), 4.23 (q, 8 H, CH_2O), 4.25 (s, 2 H, CH), 4.26 (q, 4 H, CH_2O). ^{13}C NMR, δ: 13.3 and 13.5 (both q, CH_3), 54.2 (d, CH), 58.5 (s, C), 61.4 and 61.9 (both t, CH_2O), 166.8 and 167.2 (both s, C=O).

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Correlation NMR spectroscopy of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene

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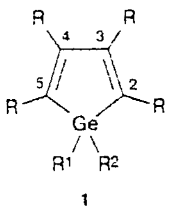
Assignment of all of the signals in the ^{1}H and ^{13}C NMR spectra of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene has been carried out using two-dimensional NMR spectroscopy.

Key words: germanium, 1-germacyclopenta-2,4-diene, ^{13}C and ^{1}H NMR spectroscopy.

1-Germacyclopenta-2,4-dienes (germoles) constitute an interesting class of organogermanium heteroaromatic compounds. However, they have been studied less extensively[1,2] than siloles, phospholes and much less extensively than pyrroles, furans, and thiophenes. The stability of germoles in the monomeric form, like that of siloles, markedly increases when alkyl or aryl substituents are introduced into the ring;[1,2] therefore, substituted metaloles are convenient objects for studying their structures by physicochemical methods. From the synthetic viewpoint, stable 2,3,4,5-tetraphenylgermoles (**1**, R = Ph) are the most accessible.



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