Complete BA→SA conversion is achieved after a period of several minutes, and the product is separated from the catalyst by vacuum distillation. After this, the catalyst can be recycled. It is likely that this is the first example of solid-phase catalytic oxidation that may be called perfect, since none of its steps requires the use of a solvent.

Experimental

BA was prepared by the previously described procedure.[4] A mechanical mixture of BA (5.7 g, $2 \cdot 10^{-4}$ mol) with the oxidant was passed through a previously described[5] worm conveyer for 10 min at room temperature. The product was distilled off *in vacuo* at 10—20 Torr, the distillate crystallized on cooling. Its melting point of 62 °C corresponds to the value reported for SA.[1] The product was identical to the authentic sample of SA prepared by oxidation of BA with $Mn(OAc)_3$ in MeCOOH.

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Electrochemical co-oxidation of C—H acids and methanol as a new route to functionalized cyclopropanes

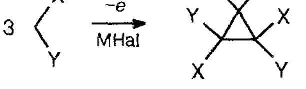
S. K. Fedukovich, M. N. Elinson, and G. I. Nikishin*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., Russian Federation.
Fax: +7 (095) 135 5328

Electrolysis of dimethyl malonate or methyl cyanoacetate in methanol in the presence of LiCl in an undivided cell leads to formation of 1,1,2,2-cyclopropanetetracarboxylic derivatives.

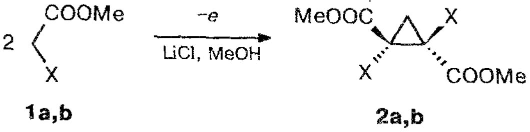
Key words: electrochemical oxidation, malonic ester, cyanoacetyc ester, 1,1,2,2-cyclopropanecarboxylic acid.

We discovered previously the reaction of electrochemical cyclotrimerization of malonic ester in methanol[1] and cyanoacetic ester in acetone[2] during electrolysis in an undivided cell in the presence of bromides and iodides of alkali metals as a mediators.



X, Y = COOMe, COOEt; M = Li, Na, K; Hal = Br, I

In this paper we established that electrolysis of malonic or cyanoacetyc esters (**1a,b**) in methanol in the presence of lithium chloride leads to formation of 1,1,2,2-cyclopropanetetracarboxylic acid derivatives (**2a,b**).



a: X = COOMe; **b**: X = CN

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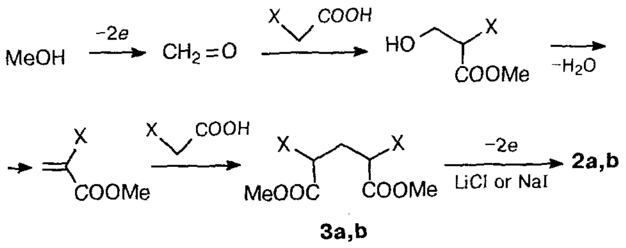
Table 1. Electrochemical co-oxidation of malonic or cyanoacetic ester **1a,b** and methanol

Expe-riment	Substrate	Electricity amount /F mol^{-1}	Conversion **1** (%)	Yield (%)[a]	
				2	**3**
1	**1a**	1.6	92	12	66
2	**1a**	3.2	100	40	—
3[b]	**1a**	2.4	100	56	—
4	**1b**	4.0	95	45	—

[a] In the experiments *1*—*3* hexamethyl 1,1,2,2,3,3-propanehexacarboxylate[3], hexamethyl 1,1,3,3,5,5-pentanehexacarboxylate and tetramethyl 2,2,4,4-tetrahydrofurantetracarboxylate[4] were identified among the by-products. [b] After passage of 1.6 F $mole^{-1}$ of electricity, 4 mmole of NaI was added to electrolyzer and electrolysis was carried out at 30 °C.

Tetramethyl 1,1,3,3-tetracarboxylate (**3a**) was also obtained by oxidation of malonic ester **1a** (Table 1, exp. *1*).

In the first step of the process direct electrooxidation of methanol at the anode provided formaldehyde, and the later hydroxymethylate C—H acid **1a,b** analogous for substituted malonic esters[5] was observed. Subsequent dehydration and addition of **1a,b** to unsaturated ester leads to methylenbismalonic ester **3a** or methylenbiscyanoacetic ester **3b**.



a: X = COOMe; b: X = CN

Thus the resulting esters **3a,b** were oxidized into cyclopropane **2a,b** according to a mechanism we have described previously[4].

The precursor of cyclopropane **2a**, the ester **3a** is formed only under the passage of 1.6 F $mole^{-1}$ of electricity. Initially formed **3a,b** after the passage of 2.4—4.0 F $mole^{-1}$ are transformed into **2a,b** and thus have never been detected among the reaction products.

The enhanced yield of **2a** in experiment *4* is caused by the greater effectiveness of NaI as a mediator of cyclization of **3a** (Ref. 4), compared to that of LiCl.

Cyclopropane **3b** was obtained only as a *trans*-isomer and identified on the basis of ^1H and ^{13}C NMR spectra[6].

The analogous reaction with malononitrile was not realized because of the high tendency of $^-CH(CN)_2$ anion to join the C≡N group with the formation of dimers, trimers and oligomers.[7,8]

Experimental

^{13}C and ^1H NMR spectra were recorded on a Bruker WM-250 (250 MHz) and Bruker AM-300 (300 MHz) in $CDCl_3$; chemical shifts were measured using tetramethylsilane as the internal standard.

"Pure" grade LiCl was dried additionally *in vacuo*. Malonic and cyanoacetic esters were distilled before using.

Esters **2a,b** were isolated by column chromatography (Silica gel L 40/100, ether—hexane, 1:1).

Tetramethyl 1,1,3,3-propanetetracarboxylate **3a** was obtained by the reaction of dimethyl malonate with formalin (yield 60 %) according to the previously described method[9].

Electrochemical co-oxidation of esters 1a,b and methanol. General method. The solution of ester **1a** or **1b** (20 mmole), LiCl (8 mmole) and MeOH (20 mL) was placed into undivided electrolyzer equipped with a Pt- or C-plate as the anode and Fe- as the cathode, magnetic stirrer, thermometer and reflux condenser. The electrolysis was carried out under a current density of 220 mA cm^{-2}, temperature of 50 °C, and passage of electricity amount as presented in Table 1. The reaction mixture was evaporated, washed with water (20 mL) and extracted with chloroform (50 mL). The organic layer was separated, dried with Na_2SO_4, evaporated and ^1H NMR spectra were measured using 1,4-dichlorobenzene as the internal standard.

Tetramethyl 1,1,2,2-cyclopropanetetracarboxylate 2a, yield 50 %, m.p. 70—71 °C. ^1H NMR, δ: 2.17 (s, 2 H, CH_2); 3.73 (s, 12 H, OMe). ^{13}C NMR, δ: 23.9 (t, CH_2); 41.1 (s, C quater.); 53.2 (q, MeO); 166.2 (C=O).

Dimethyl 1,2-dicyanocyclopropane-1,2-dicarbooxylate 2b, yield 40 %, m.p. 131—132 °C. ^1H NMR, δ: 2.60 (s, 2 H, CH_2); 3.97 (s, 6 H, OMe). ^{13}C NMR, δ: 25.6 (t, CH_2); 28.2 (s, C quater.); 53.8 (q, OMe); 112.1 (s, C≡N); 162.0 (C=O).

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