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Electrochemically Induced Oxidative Rearrangement of Alkylidenemalonates

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Abstract: Alkylidenemalonates capable of double bond migration being electrolyzed in methanol or ethanol in the presence of alkali metal halides in an undivided cell equipped with Fe cathode are transformed into 2-alkyl-3,3-dimethoxyalkane-1,1-dicarboxylates in 70-90% yield via electrochemically induced oxidative rearrangement. Acidification of the reaction mixture after the electrolysis leads to the formation of 2-alkyl-3-oxoalkane-1,1-dicarboxylates. In the case of isobutylidenemalonate, the electrolysis intermediate dimethyl 3,3-dimethyl-2-methoxy-cyclopropane-1,1-dicarboxylate was isolated in 70% yield.

Alkylidenemalonates are well-known useful intermediates in organic synthesis, mainly due to the reactions of their double bond which is activated by conjugation with two carboxylate groups.[1]

The known electrochemical transformations of alkylidenemalonates are also connected with two types of reactivity of the activated double bond: reductive hydrodimerization of alkylidenemalonates[2,3] and addition of electrochemically generated anions to the double bond of alkylidenemalonates.[4,5]

In the last few years mediators were widely used for the electrooxidation and electroreduction of organic compounds.[6] Among a variety of mediators, the redox system halide anion - halogen is one of the most useful from the viewpoint of organic synthesis and large-scale processes.[7]

Recently, in the course of our study on the electrochemical oxidation of organic compounds in the presence of alkali metal halides, we have carried out electrochemical cyclodimerization of alkylidenemalonates into 3,4-disubstituted cyclobutane-1,1,2,2-tetracarboxylates[3,8] and electrocatalytic transformation of alkylidenemalonates into 2-alkyl-3,3-dimethoxyalkane-1,1-dicarboxylates via

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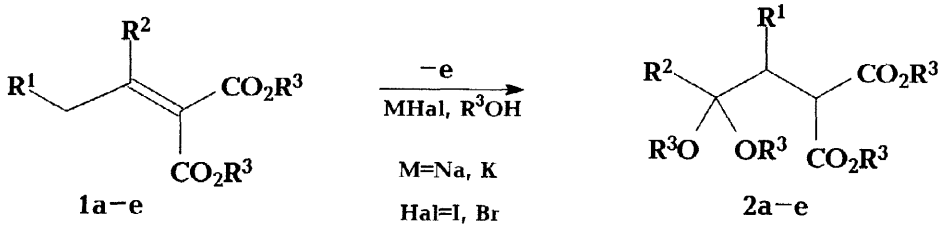
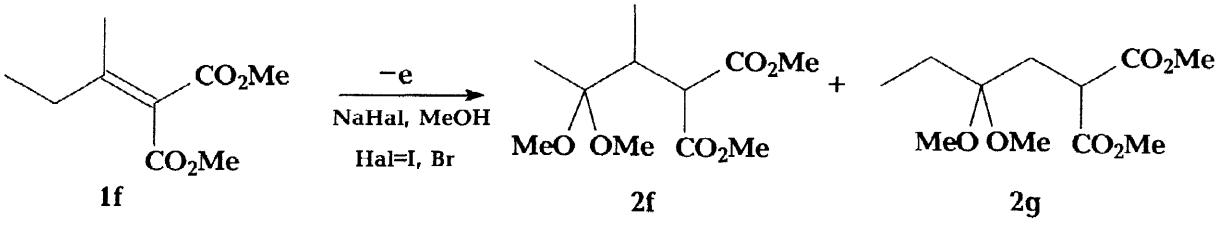
electrochemically induced oxidative rearrangement.[9] The present paper is concerned with a detailed study of the last process in order to estimate its scope and limitations.

Electrolysis of alkylidenemalonates in methanol or ethanol in the presence of alkali metal halides as mediators, was carried out in an undivided cell with a Pt anode and an Fe cathode under constant current density. Under these conditions alkylidenemalonates **1a-e** having allylic hydrogen atoms were transformed into 3,3-dialkoxypropane-1,1-carboxylates **2a-e** with rearrangement of the structure of the starting compound (table 1):



a $R^1=R^2=H$, $R^3=Me$
b $R^1=Me$, $R^2=H$, $R^3=Me$
c $R^1=Me$, $R^2=H$, $R^3=Et$
d $R^1=Et$, $R^2=H$, $R^3=Me$
e $R^1=H$, $R^2=Me$, $R^3=Me$

Electrolysis of **1f** resulted in the formation of both the "normal" product **2f** and the rearrangement product **2g** in 18 and 54% yields, respectively:



It has been found that sodium iodide is the best mediator for the process and using this mediator, esters **2a-e** were obtained in 70-90% yield. With potassium iodide as mediator, the yields of the rearrangement products decreased by 10-15%. Replacement of sodium iodide by sodium bromide caused a more significant decrease of the rearrangement product yields (down to 50%).

Electrolysis of **1a-e** in the absence of a halogen anion with $NaClO_4$ as the electrolyte does not afford rearrangement compounds **2a-e**. The main process of the **1a-e** electrolysis in the presence of $NaClO_4$ under the conditions studied is the electrochemically induced addition of methanol to the double bond of alkylidenemalonates with the formation of 2-methoxysubsituted alkane-1,1-dicarboxylates.

Table 1. Electrooxidation of alkylidenemalonates.

N	Substrate	R^1	R^2	R^3	Mediator	Electricity passed, F/mol	Conversion of substrate [%]	Rearrangement product, yield [%][b]	Other products, yield [%][c]
1	**1a**	H	H	Me	NaI	2.0	100	**2a**, 78 (78)	**3a**, 5; **4a**, 9
2	**1a**	H	H	Me	KI	2.0	100	**2a**, 72 (72)	**3a**, 6; **4a**, 8
3	**1a**	H	H	Me	NaBr	2.0	100	**2a**, 48 (48)	**3a**, 8; **4a**, 5
4	**1b**	Me	H	Me	NaI	2.2	99	**2b**, 80 (73)	**3b**, 8; **4b**, 4
5	**1b**	Me	H	Me	KI	2.2	98	**2b**, 73 (65)	**3b**, 9; **4b**, 2
6	**1c**[d]	Me	H	Et	NaI	2.2	88	**2c**, 72 (58)	**3c**, 6
7	**1d**	Et	H	Me	NaI	2.2	100	**2d**, 80 (73)	**3d**, 6; **4c**, 8
8	**1d**	Et	H	Me	KI	2.3	100	**2d**, 73 (63)	**3d**, 8; **4c**, 5
9	**1e**	H	Me	Me	NaI	2.8	99	**2e**, 89 (63)	**3e**, 3
10	**1e**	H	Me	Me	KI	2.8	97	**2e**, 81 (56)	**3e**, 5
11	**1e**[e]	H	Me	Me	NaI	2.9	100	**5c**, 64 (50)	**3e**, 2
12	**1f**	Me	Me	Me	NaI	6.0	92	**2f**[f], 54; **2g**, 18 (22)[g]	—
13	**1f**	Me	Me	Me	NaBr	6.0	70	**2f**[f], 43; **2g**, 14 (13)[g]	—
14	**6**	$(CH_2)_4$		Me	NaI	3.0	92	**7**, 61; **8**, 19 (54)[g]	—

[a] 30 mmol of substrate, 15 mmol of mediator in 45 ml of MeOH, Pt-anode, Fe-cathode, current density 200 mA/cm^2, at 60°C.

[b] Isolated yields, in parenthesis current yields.

[c] Determined by gas chromatography and NMR spectroscopy.

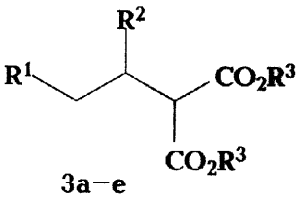
[d] EtOH as a solvent.

[e] After electrolysis the reaction mixture was acidified with HCl to pH 6.0.

[f] Isolated as a mixture of **2f** and **2g**.

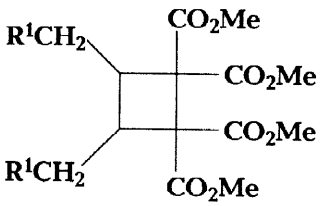
[g] Total current yield of two products.

By-products of the reactions were alkylmalonates **3a-e** and also 3,4-dialkylcyclobutane-1,1,2,2-tetracarboxylates **4a-c** (for the starting compounds with $\mathbf{R^2}$=H) with an overall yield of less than 15%.



3a–e

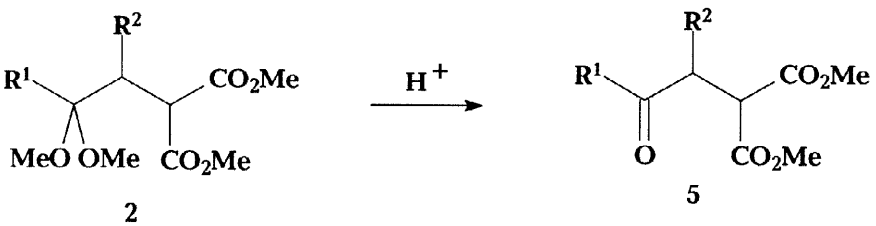
a $R^1=R^2=H$, $R^3=Me$
b $R^1=Me$, $R^2=H$, $R^3=Me$
c $R^1=Me$, $R^2=H$, $R^3=Et$
d $R^1=Et$, $R^2=H$, $R^3=Me$
e $R^1=H$, $R^2=Me$, $R^3=Me$



4a–c

a $R^1=H$
b $R^1=Me$
c $R^1=Et$

Acidification of the reaction mixture after the electrolysis resulted in hydrolysis of the rearrangement products 2 with the formation of carbonyl compounds **5**:



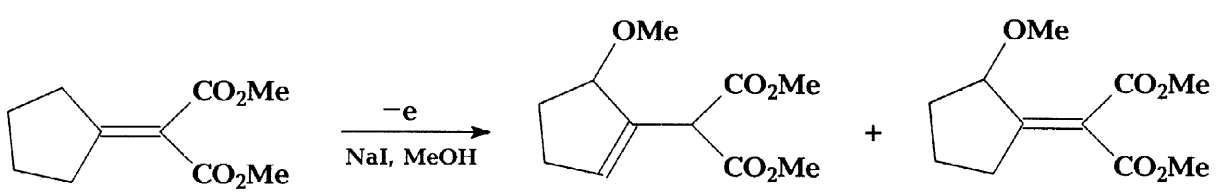
2

a $R^1=R^2=H$
b $R^1=Me$, $R^2=H$
e $R^1=H$, $R^2=Me$
f $R^1=R^2=Me$

5

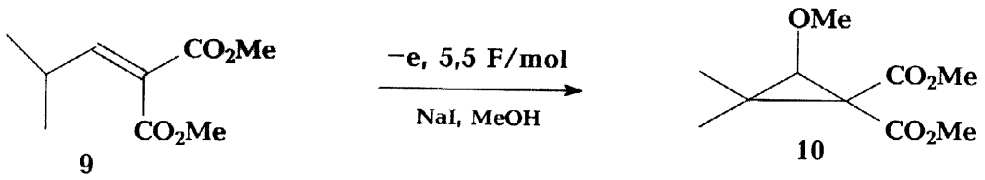
a $R^1=R^2=H$
b $R^1=Me$, $R^2=H$
c $R^1=H$, $R^2=Me$
d $R^1=R^2=Me$

Under the conditions used, cyclopentylidenemalonate **6** afforded two isomeric methoxylated compounds 7 and **8** in 61% and 22% yields, respectively:



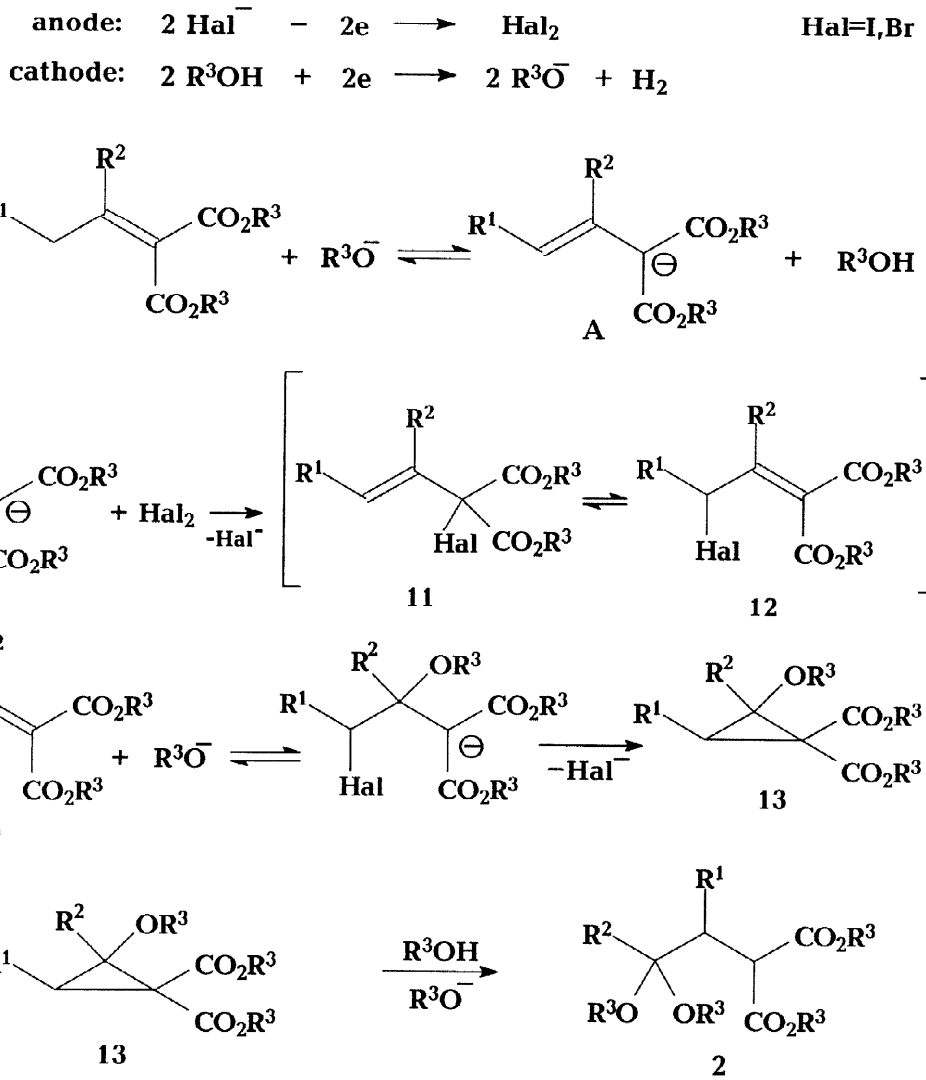
6 7 8

The most interesting result was found with electrolysis of isobutylidenemalonate **9**. In this case 3,3-dimethyl-2-methoxycyclopropane-1,1-dicarboxylate **10** was isolated from the reaction mixture in 70% yield.



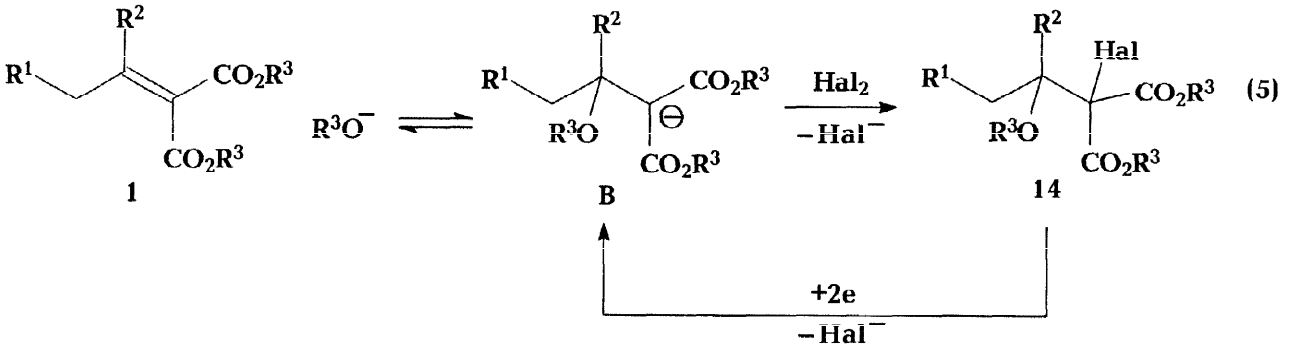
Current efficiency of alkylidenemalonate electrooxidation decreases with increasing the number of alkyl substituents at the double bond of alkylidenemalonates and also with the change of linear alkyl substituents for branched ones. Thus, in the row **1a** > **1b**, **1d** > **1e** > **6** > **1f** the current efficiency of the electrooxidation decreases by nearly three times.

Taking into consideration all of the above mentioned data, the following general mechanism of the electrochemical oxidative rearrangement is suggested:



Scheme 1

Formation of **A**-type anions by the action of alkoxide anion on alkylidenemalonates (equation 1) has been established earlier.[10] The side reaction at this stage is a reversible addition of alkoxide anion to the double bond of alkylidenemalonates **1a-e**, equation (**5**).[11] It should also be mentioned that compounds of type **14**, which could also be formed under the conditions studied, are sufficiently stable in chemical transformations, but are very easily reduced at the cathode with regeneration of **B**-type anion:[12]



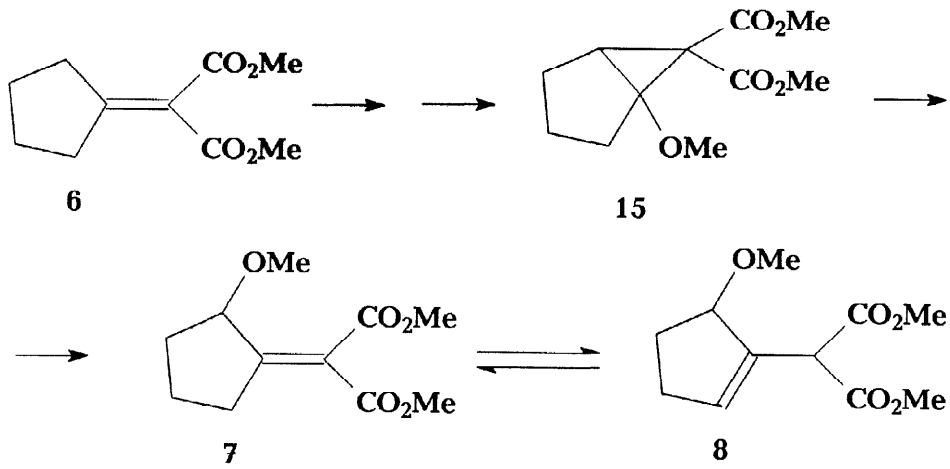
(5)

Reaction of **A**-type anions with halogen generated at the anode results in the formation of halogen substituted esters **11** and **12** (equation 2). In the case of **Hal** = **I**, allylic iodide **11** is easily isomerized into allylic iodide **12**.[13] Rearrangement of this type is also known for allylic bromides,[13] but the rate of the rearrangement in the latter case is slower. This fact could explain the decreasing yields of the rearranged compounds **2** when bromide anions are used as the mediator.

The interaction of allylic bromide **12** with alkoxide ions in alcohols, as it has been established earlier, results in the formation of the unstable intermediate cyclopropane **13** which undergoes C-C bond cleavage in alcohols giving rise to the end products of the reactions - compounds **2**.[14]

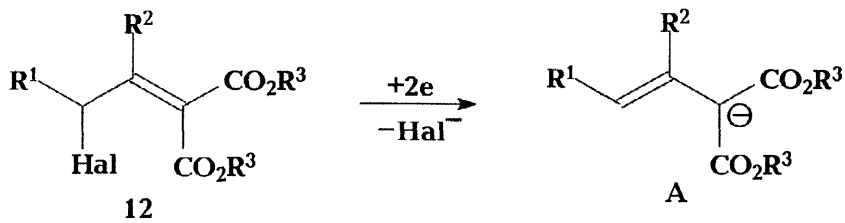
Only in the case of the electrochemical oxidation of isobutylidenemalonate **9** was the relatively stable cyclopropane **10** isolated. The same result was also obtained in the chemical reaction of (2-bromo-isopropylidene)malonate with methoxide anion in methanol.[15] Cyclopropane **10** is more stable mainly due to the presence of the two Me groups at $C_{(3)}$, which increases steric hindrance to any chemical attack on the cyclopropane ring. This effect of two Me groups on the cyclopropanes stability has previously been demonstrated for several types of cyclopropane compounds.[16]

Taking into consideration the above, it is possible now to explain the result of the electrooxidation of cyclopentylidenemalonate **6** into ester **8** as an isomerization of intermediate cyclopropane **15** under the electrolysis conditions:



The main side reactions of **1a-e** electrooxidation under the conditions studied were cathodic reduction of the double bond with the formation of alkylmalonates **3a-e** and generation of cyclodimerization products **4a-c** (table 1).

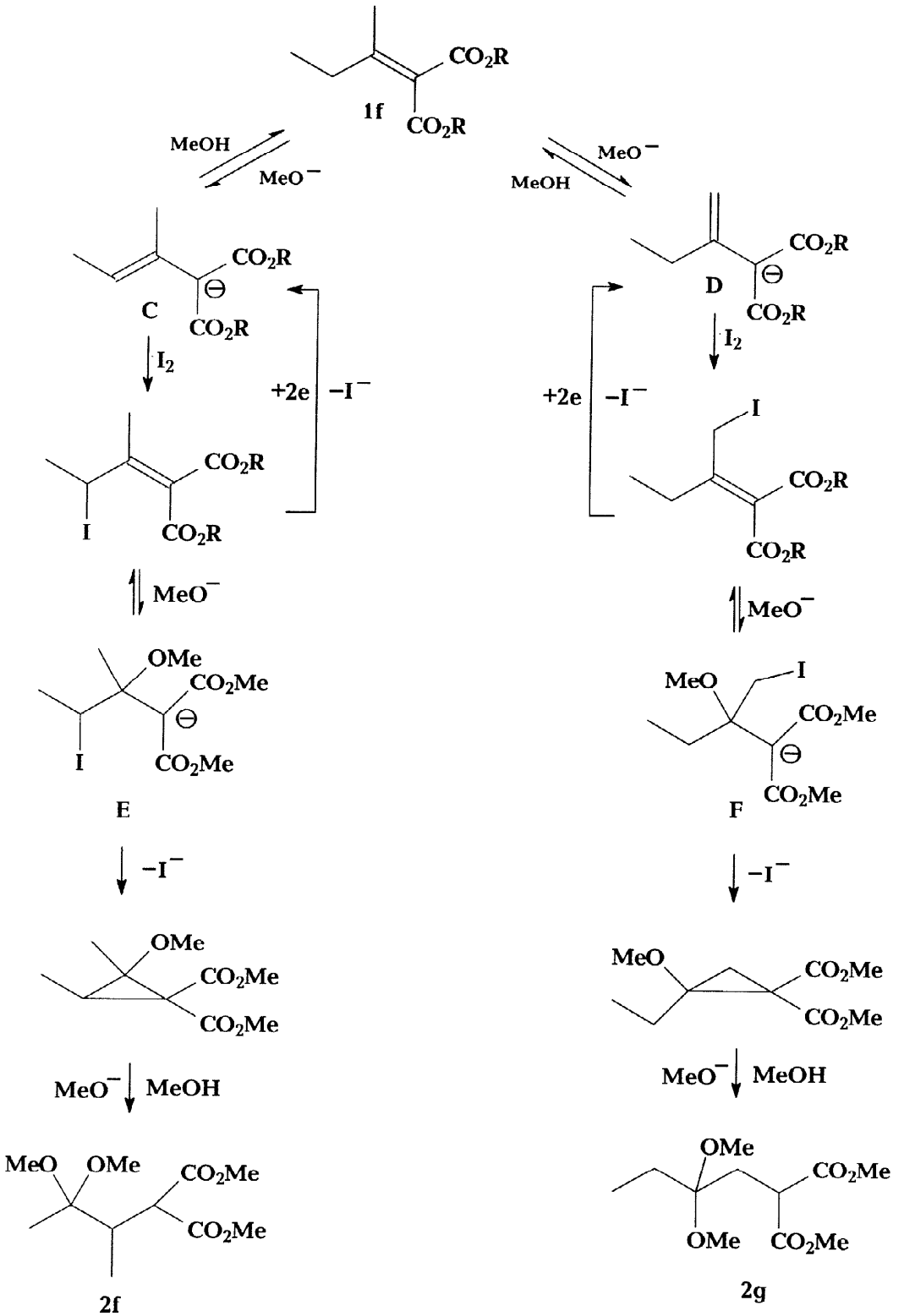
One additional side process under the conditions studied was cathodic reduction of the allylic halogen substituted esters **12.** This reaction is an alternative to the reaction stated in equation **(3)** and takes place to a sufficient extent for alkylidenemalonates with two alkyl substituents at the double bond and isobutylidenemalonate **9** when the reaction of alkoxide anion addition to the double bond is hindered or steric reasons:



(6)

As the result of the reaction **(6)** is regeneration of anion **A** , its influence on the whole process of the oxidative rearrangement of alkylidenemalonates **1e,f, 6** and **9** only resulted in decreasing the current yield of rearranged products.

The reaction of **1f** with alkoxide anions leads to the formation of two anions **C** and **D** (scheme 2), which then afford two different allylic iodides. In the first stage, a more thermodynamically stable anion **C** having trisubstituted double bond should be formed predominantly. On the other hand, cyclization in the sterically less hindered anion **F**, having a primary iodide, should occur more rapidly compared with anion **E**, having a secondary iodide. The last reaction is probably the rate-determining step of the whole process and this is a reason for ester **2g** to be a preferable product in the **1f** oxidative rearrangement. As follows from scheme 2, the formation of anions **C** and **D** is reversible and transformation of anion **E** into anion **F** under the conditions of electrolysis takes place as a result of the action of the rate-determining step.



Scheme 2

Experimental

GLC analyses were carried out on LKhM-80 chromatography with a flame-ionization detector. Columns: 1) glass column 3 m x 3 mm with 5% OV-17 on Inerton (0.16-0.20 mm) 2) glass column 3 m x 3 mm with 10% FFAP on Chromaton N-Super (0.13-0.16 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker WM-250 (250 MHz) or Bruker AM-300 (300 MHz) spectrometers. Chemical shifts are presented on the δ scale with tetramethylsilane (TMS) used as the internal standard.

Alkylidenemalonates **1a-f** were prepared by the condensation of malonate with the corresponding aldehydes or ketones according to a known procedure.[17] Alkylmalonates **3a-e** were obtained by alkylation of malonates with a corresponding alkyl halides.[18] 3,4-Dialkylcyclobutane-1,1,2,2-tetracarboxylates **4a-c** were synthesized by the electrochemical cyclodimerization method.[3]

General electrolysis procedure.

A solution of **1** (30 mmol) and sodium halide (15 mmol) in methanol (45 ml) was electrolyzed in an undivided cell equipped with a Pt-anode and an Fe-cathode at 60^{0}C under constant current density 200 mA/cm^2 until the quantity of the electricity indicated in Table 1 was passed. The solvent was then removed and the residue extracted with chloroform or ether, washed with an aqueous solution of $Na_2S_2O_3$, and dried with Na_2SO_4 (procedure A). After distillation compounds **2**, **7**, **8** **10** were isolated. In some cases, the reaction mixture after the electrolysis was acidified with dilute aqueous HCl to pH 5.5-6.0 (procedure B), and after neutralization and standard treatment, compounds **5a-d** were isolated.

Dimethyl 3,3-dimethoxypropane-1,1-dicarboxylate (**2a**)[14], b. p. 67-68^{0}C (0.03 torr), ^{1}H NMR ($CDCl_3$): 2.19 (dd, 2H, CH_2 J_1=7.2 Hz, J_2=5.4 Hz), 3.29 (s, 6H, CH_3O), 3.50 (t, 1H, C<u>H</u>(COOMe)$_2$, J=7.2 Hz), 3.71 (s, 6H, CH_3O), 4.38 (t, 1H, C<u>H</u>(OMe)$_2$, J=5.4 Hz). ^{13}C NMR ($CDCl_3$): 31.6 (t), 47.1 (d), 52.1 (q), 53.1 (q), 102.3 (d), 169.2 (s). Anal. Calcd. for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 48.78; H, 7.23.

Dimethyl 3,3-dimethoxy-2-methylpropane-1,1-dicarboxylate (**2b**)[14], b. p. 125-127^{0}C (10 torr), ^{1}H NMR ($CDCl_3$): 0.98 (d, 3H, CH_3 J=6.8 Hz), 2.55 (m, 1H, C<u>H</u>Me), 3.31 (s, 3H, CH_3O), 3.33 (s, 3H, CH_3O), 3.50 (d, 1H, C<u>H</u>(COOMe)$_2$ J=5.2 Hz), 3.70 (s, 6H, CH_3O), 4.26 (d, 1H, C<u>H</u>(OMe)$_2$ J=7.3 Hz). ^{13}C NMR ($CDCl_3$): 12.1 (q), 36.4 (d), 52.1 (q), 52.2 (q), 52.9 (d), 53.7 (q), 55.2 (q), 106.4 (d), 169.0 (s) 169.3 (s). Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.16; H, 7.63.

Diethyl 3,3-diethoxy-2-methylpropane-1,1-dicarboxylate (**2c**)[19], b. p. 101-103^{0}C (0.2 torr), ^{1}H NMR ($CDCl_3$): 0.98 (d, 3H, CH_3 J=6.8 Hz), 1.13 (t, 6H, CH_3 J=7.0 Hz), 1.22 (t, 6H, CH_3 J=7.1 Hz), 2.49 (m, 1H, C<u>H</u>Me),

3.46 (d, 1H, CH(COOEt)$_2$ J=5.2 Hz), 3.45 (m, 2H, CH_2O), 3.62 (m, 2H, CH_2O), 4.13 (q, 4H, OCH_2 J=7.0 Hz), 4.39 (d, 1H, CH(OEt)$_2$ J=7.3 Hz). ^{13}C NMR ($CDCl_3$): 12.0 (q), 14.1 (q), 15.2 (q), 37.1 (d), 53.6 (d), 61.1 (t), 62.3 (t), 63.5 (t), 104.4 (d), 168.8 (s), 169.0 (s). Anal. Calcd. for $C_{14}H_{26}O_6$: C, 57.91; H, 9.03. Found: C, 58.01; H, 8.98.

Dimethyl 2-ethyl-3,3-dimethoxy-propane-1,1-dicarboxylate (**2d**)[14], b. p. 71-72^{0}C (0.04 torr), ^{1}H NMR ($CDCl_3$): 0.90 (t, 3H, CH_3 J=6.2 Hz), 1.32-1.66 (m, 2H, CH_2), 2.40 (m, 1H, $CHCH_2$), 3.30 (s, 3H, CH_3O), 3.35 (s, 3H, CH_3O), 3.57 (d, 1H, CH(COOMe)$_2$ J=5.1 Hz), 3.68 (s, 6H, CH_3O), 4.40 (d, 1H, CH(OMe)$_2$ J=7.4 Hz). ^{13}C NMR ($CDCl_3$): 11.6 (q), 20.5 (t), 42.9 (d), 51.0 (d), 51.9 (q), 53.6 (q), 55.5 (q), 105.8 (d), 169.1 (s) 169.3 (s). Anal. Calcd. for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 52.98; H, 8.03.

Dimethyl 3,3-dimethoxylbutane-1,1-dicarboxylate (**2e**), b. p. 89-92^{0}C (0.15 torr), ^{1}H NMR ($CDCl_3$): 1.21 (s, 3H, CH_3), 2.27 (d, 2H, CH_2 J=7.2 Hz), 3.13 (s, 6H, CH_3O), 3.47 (t, 1H, CH J=7.2 Hz), 3.71 (s, 6H, CH_3O). ^{13}C NMR ($CDCl_3$): 20.6 (q), 35.4 (t), 47.7 (d), 48.9 (q), 52.4 (q), 100.2 (s), 169.8 (s). Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.03; H, 7.68.

Dimethyl 3,3-dimethoxy-2-methylbutane-1,1-dicarboxylate (**2f**) was isolated as a mixture with ester **2g** in a ratio of 1:3, b. p. 96-103^{0}C (0.15 torr), ^{1}H NMR ($CDCl_3$) for **2f** after excluding signals of **2g** (NMR for **2g** cf. below): 0.91 (d, 3H, CH_3 J=6.8 Hz), 1.17 (s, 3H, CH_3), 2.46 (m, 1H, CHMe), 3.06 (s, 3H, CH_3O), 3.09 (s, 3H, CH_3O), 3.51 (d, 1H, CH(COOMe)$_2$ J=5.3 Hz), 3.70 (s, 3H, CH_3O), 3.71 (s, 3H, CH_3O). ^{13}C NMR ($CDCl_3$): 12.4 (q), 20.8 (q), 37.2 (d), 51.8 (q), 52.1 (q), 53.1 (d), 54.9 (q), 55.3 (q), 101.2 (s), 169.6 (s), 169.8 (s). Anal. Calcd. for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 53.06; H, 8.17.

Dimethyl 3,3-dimethoxypentane-1,1-dicarboxylate (**2g**) was isolated from the aforementioned mixture of **2f** and **2h** as viscous liquid by silica gel column chromatography (ether-hexane 1:2), ^{1}H NMR ($CDCl_3$): 0.78 (t, 3H, CH_3 J=6.5 Hz), 1.54 (q, 2H, CH_2 J=6.5 Hz), 2.23 (d, 2H, CH_2 J=7.4 Hz), 3.08 (s, 6H, CH_3O), 3.39 (t, 1H, CH J=7.4 Hz), 3.68 (s, 6H, CH_3O). ^{13}C NMR (CDC_3): 9.1 (q), 31.6 (t), 34.9 (t), 48.3 (d), 49.0 (q), 52.5 (q), 107.9 (s), 169.9 (s). Anal. Calcd. for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 53.15; H, 8.23.

Dimethyl 3-oxopropane-1,1-dicarboxylate (**5a**), b. p. 72-73^{0}C (0.1 torr), ^{1}H NMR ($CDCl_3$): 3.18 (d, 2H, CH_2, J=7.5 Hz), 3.71 (s, 6H, CH_3O), 3.82 (t, 1H, CH, J=7.4 Hz), 9,64 (s, 1H, CH=O). ^{13}C NMR ($CDCl_3$): 41.6 (t), 45.9 (d), 52.8 (q), 169.2 (s), 200.8 (d). Anal. Calcd. for $C_7H_{10}O_5$: C, 48.28; H, 5.79. Found: C, 48.05; H, 5.63.

Dimethyl 2-methyl-3-oxopropane-1,1-dicarboxylate (**5b**), b. p. 68-70^{0}C (0.05 torr), ^{1}H NMR ($CDCl_3$): 1.33 (d, 3H, CH_3, J=6.7 Hz), 3.21 (m, 1H, CH), 3.73 (s, 6H, CH_3O), 3.77 (d, 1H, CH, J=6.2 Hz), 9.65 (s, 1H, CH=O). ^{13}C NMR ($CDCl_3$): 11.8 (q), 50.4 (d), 52.3 (d), 52.9 (q), 169.2 (s), 169.5 (s), 202.4 (d). Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 49.83; H, 6.24.

Dimethyl 2-ethyl-3-oxopropane-1,1-**dicarboxylate (5c)**, b. p. 76-78^{0}C (0.04 torr), ^{1}H NMR ($CDCl_3$): 1.17 (t, 3H, CH_3, *J*=6.7 Hz), 1.52-1.83 (m, 2H, CH), 3.15 (m, 1H, CH), 3.75 (s, 1H, CH_3O), 3.81 (d, 1H, CH, *J*=6.2 Hz), 9,63 (s, 1H, C<u>H</u>=O). ^{13}C NMR ($CDCl_3$): 11.7 (q), 20.3 (t), 47.5 (d), 52.8 (q), 53.5 (d), 168.4 (s), 169.3 (s), 202.5 (d). Anal. Calcd. for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.21; H, 6.74.

Dimethyl 3-oxobutane-1,1-dicarboxylate (**5d**), b. p. 82-84^{0}C (0.15 torr), ^{1}H NMR ($CDCl_3$): 2.25 (s, 3H, CH_3), 3.05 (d, 2H, CH_2, *J*=7.5 Hz), 3.72 (s, 6H, CH_3O), 3.88 (t, 1H, CH, *J*=7.5 Hz), 9,65 (s 1H, C<u>H</u>=O). ^{13}C NMR ($CDCl_3$): 29.3 (q), 41.8 (t), 46.3 (d), 52.7 (q), 169.0 (s), 204.6 (s). Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 49.89; H, 6.28.

Dimethyl (5-methoxycyclopent-1-enyl)malonate (**7**) was isolated as a viscous liquid by silica gel column chromotography (eluent ether-hexane 2:1), ^{1}H NMR ($CDCl_3$): 1.72 (m, 2H, CH_2), 2.05-2.30 (m, 2H, CH_2), 3.24 (s, 3H, CH_3O), 3.72 (s, 3H, CH_3O), 3.74 (s, 3H, CH_3O), 4.29 (s, 1H, C<u>H</u>$(COOMe)_2$), 4.46 (m, 1H, C<u>H</u>OMe), 5.96 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$): 28.8 (t), 30.2 (t), 50.7 (d), 52.3 (q), 52.4 (q), 55.7 (q), 86.1 (d), 133.7 (d), 135.6 (s), 168.1 (s), 168.3 (s). Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.72; H, 7.01.

Dimethyl 2-methoxycyclopentylidenemalonate (**8**), was isolated as a viscous liquid by silica gel column chromotography eluent (ether-hexane 2:1), ^{1}H NMR ($CDCl_3$): 2.74-2.84 (m, 6H, CH_2), 3.30 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O), 3.78 (s, 3H, CH_3O), 4.41 (m, 1H, C<u>H</u>OMe). ^{13}C NMR ($CDCl_3$): 25.7 (t), 31.7 (t), 34.2 (t), 51.8 (q), 51.9 (q), 53.9 (q), 82.2 (d), 119.5 (s), 128.7 (s), 163.9 (s), 164.9 (s). Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.65; H, 7.05.

Dimethyl 3,3-dimethyl-2-methoxycyclopropane-1,1-dicarboxylate (**10**)[14,15], b. p. 48-49^{0}C (0.06 torr), ^{1}H NMR ($CDCl_3$): 1.19 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 3.48 (s, 3H, CH_3O), 3.63 (s, 1H, CH), 3.70 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O). ^{13}C NMR ($CDCl_3$): 16.6 (q), 19.6 (q), 31.7 (s), 41.9 (s), 52.2 (q), 52.3 (q), 58,7 (q), 72.2 (d), 166.1 (s), 168.5 (s). Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.36; H, 7.49

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