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Electrochemical Cyclodimerization of Alkylidenemalonates into 3,4-Disubstituted Cyclobutane-1,1,2,2-tetracarboxylates

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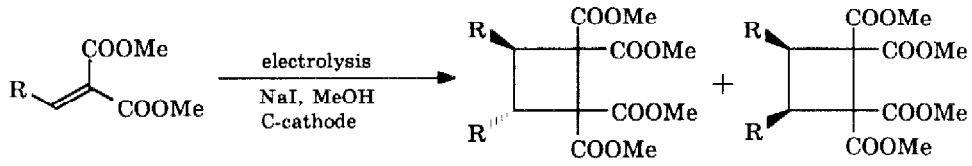
Key words: Alkylidenemalonates; cyclobutane-1,1,2,2-tetracarboxylates; cyclodimerization; electrolysis, mediators

Abstract: *Alkylidenemalonates being electrolyzed in methanol in undivided cell with glassy carbon, carbon or lead cathode in the presence of sodium iodide or sodium bromide are transformed into 3,4-disubstituted cyclobutane-1,1,2,2-tetracarboxylates.*

Ultra-violet irradiation of conjugated olefins with acceptor groups results in formation of substituted cyclobutanes[1-3].

In the course of our investigations on synthetic utility of alkali metal halides as mediators in electrooxidation of organic compounds[4-8] we have found the electrochemical cyclodimerization of alkylidenemalonates **1a-e** into 3,4-disubstituted cyclobutane-1,1,2,2-tetracarboxylates **2a-e** and **3a-e** (Table):



1a-e **2a-e** **3a-e**

a R=Me, b R=Et, c R=n-Pr, d R=Me$(CH_2)_6$, e R=Ph

Table. Electrochemical cyclodimerization of alkylidenemalonates **1a-e** [a]

Substrate	Electrolyte	Electricity passed F/mol	Products, yield (%)[b]	
1a	NaI	7.0	**2a**, 42;	**3a**, 31
1a	NaBr	7.0	**2a**, 33;	**3a**, 21
1b	NaI	5.0	**2b**, 39;	**3b**, 30
1c	NaI	3.7	**2c**, 32;	**3c**, 26
1d	NaI	4.0	**2d**, 28;	**3d**, 24
1e	NaI	6.0	**2e**, 42;	**3e**, 14
1a [c]	NaI	7.0	**2a**, 35;	**3a**, 23
1a [d]	NaI	7.0	**2a**, 28;	**3a**, 17

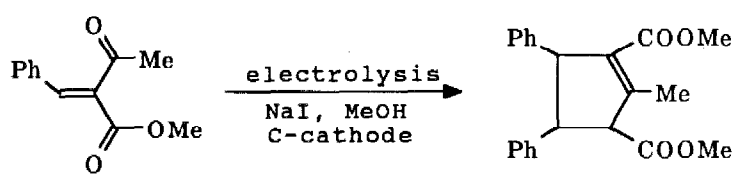
[a] 10 mmoles of **1a-e** and 7 mmoles of electrolyte in 20 ml of MeOH, glassy-carbon cathode, Pt-anode, constant current density 80 mA/cm^2, 60° C. [b] Determined by GLC and/or ^{1}H NMR, conversion of **1a-d** - 100%, **1e** - 93%. Preparative yields of some isolated products are shown in the ***Typical procedure*** [c] Carbon cathode. [d] Lead cathode.

Cyclobutanes **2a** and **3a** were obtained with lesser yields with usual carbon and lead cathodes or with sodium bromide as electrolyte.

The main by-processes are hydrogenation of **1a-e** into alkylmalonates (5-20% yield) and oxidative transformation of **1a-e** into 2-alkyl-3,3-dimethoxyalkane-1,1-dicarboxylates via rearrangement[9] in 10-35% yield. The amount of by-products increases with the length of substituent R in **1a-d**. Electrolysis of **1a-e** under the conditions of electrochemical oxidative rearrangement[9] (Fe-cathode, constant current density 220 mA/cm^2) results in formation of **2a-e** and **3a-e** only in 1-5% yield.

Diphenylmethylenemalonate, cyclopentylidenemalonate and iso-propylidenemalonate gave no cyclic products of type **2** and **3** under conditions used.

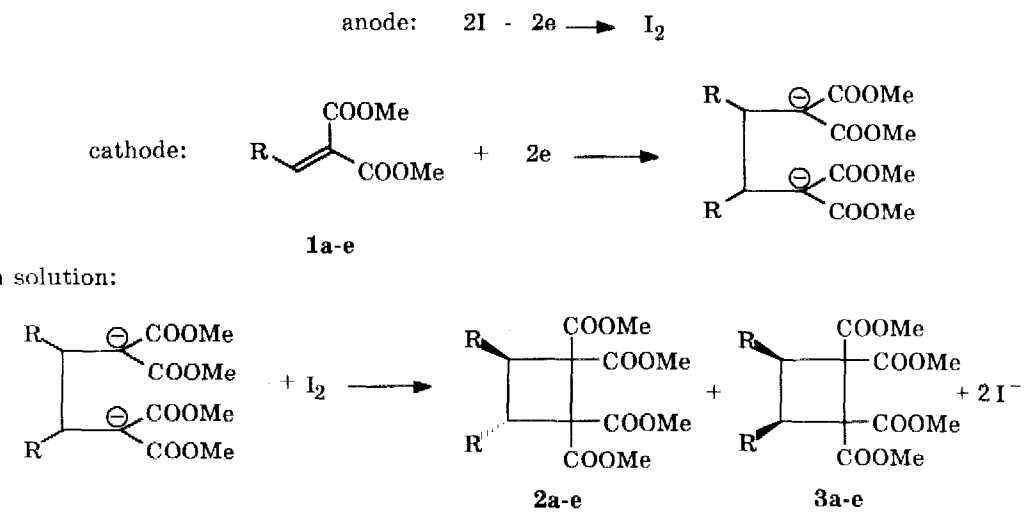
Electrolysis of benzylideneacetoacetate **4** under the same conditions results in formation of cyclopentene **5** in 56% yield:



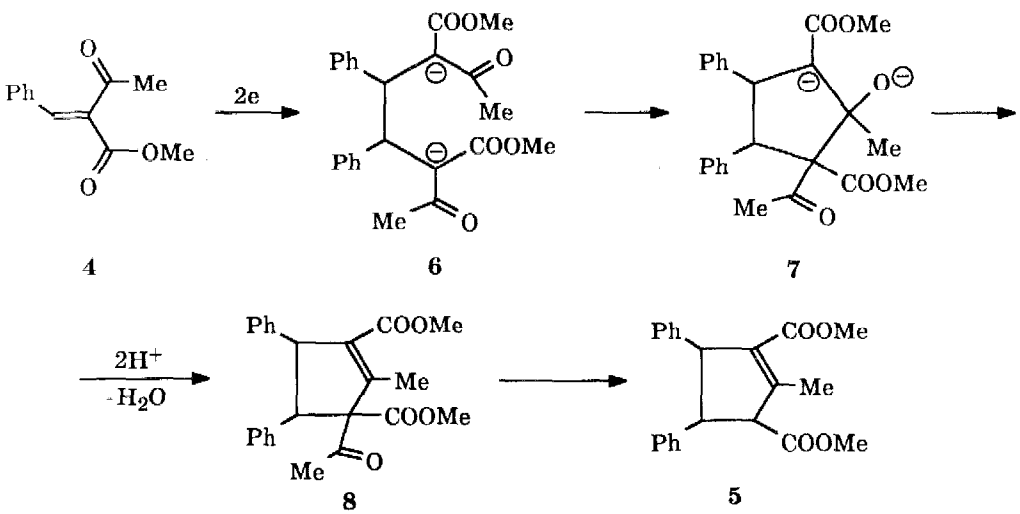
4 **5**

Electrolysis of **1e** in the presence of $NaClO_4$ leads to *d,l-* and *meso-* $(MeOOC)_2CHCHPhCHPhCH(COOMe)_2$ in 37% and 28% yield. This mixture being electrolyzed in the presence of NaI are transformed into **2e** and **3e** in 41% and 22% yield respectivly.

The suggested reaction mechanism involves:



In the case of **4** dianion **6** formed at cathode undergoes intermolecular cyclization into **7** with subsequent protonation, and dehydration into **8**. Under conditions of electrolysis the cleavage of β-ketoester **8** leads to **5**.



Typical procedure. A solution of **1a-e** or **4** (10 mmol) and NaI (7 mmol) in 20 ml of MeOH was electrolyzed in the undivided cell equipped with Pt-anode and carbon, glassy carbon or lead cathode at 60° under constant current density of 80 mA/cm^2 (quantity of electricity passed is presented in Table). The solvent was removed, the residue was extracted with $CHCl_3$, the extract was washed with solution of $Na_2S_2O_3$,, dried with Na_2SO_4, concentrated

and analyzed by GLC and NMR (see Table). The residue was crystallized from methanol or ether-hexane mixture, or purified by column chromatography on silicagel with eluant ether-hexane (1:2); eluted first were **3a-e**, eluted second were **2a-e**[10]. Some of the isolated products are listed below: **2a**, yield 31%, m.p. 155-157° (sealed tube). **2b**, yield 30%, m.p. 112-113°. **2e**, yield 35%, m.p. 151-152°. **3a**, yield 25%, oil, n_D^{24} 1.4651. **3b**, yield 18%, m.p. 74-75°.[11]

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10. All compounds gave satisfactory elemental analysis and spectroscopic data [^1H (250MHz) and ^{13}C (75 MHz) NMR]. Structures of **2a** and **2e** were confirmed by X-ray crystallographic analysis. The assignment of trans-configuration of **2b-d** was perfomed on the basis of the similarity of NMR spectra of dialkyl substituted **2a** and **2b-d**. It is of note, that ^1H NMR ($CDCl_3$) signals for methine protons of CH-groups of *cis*-isomers **3a-d** are shifted by 0.18-0.28 ppm downfield relative to analogous signals of the corresponding *trans*-isomers **2a-d**, δ (ppm): **2a**, 2.85, **3a**, 3.13; **2b**, 2.74, **3b**, 2.93; **2c**, 2.81, **3c**, 2.99; **2d**, 2.81, **3d**, 2.99. ^{13}C NMR ($CDCl_3$) signals of CH-groups of **3a-d** are shifted by 2.7-3.3 ppm upfield relative to those of the corresponding **2a-d**, δ (ppm): **2a**, 39.7, **3a**, 36.3; **2b**, 45.4, **3b**, 43.7; **2c**, 43.5, **3c**, 41.6; **2d**, 43.4, **3d**, 41.6.
11. **2a**: ^1H NMR ($CDCl_3$), δ: 1.00 (6H, m), 2.85 (2H, m), 3.71 and 3.73 (12H, each s) ppm; ^{13}C NMR ($CDCl_3$), δ: 14.41 (q), 39.71 (d), 52.32 (q), 52.50 (q), 61.82 (s), 168.42 (s), 169.64 (s) ppm.

    2b: ^1H NMR ($CDCl_3$), δ: 0.92 (6H, t), 1.40 (4H, m), 2.74 (2H, m), 3.71 and 3.73 (12H, each s) ppm; ^{13}C NMR ($CDCl_3$), δ: 11.98 (q), 24.74 (t), 45.40 (d), 53.38 (q), 52.51 (q), 56.42 (s), 168.74 (s), 169.91 (s) ppm.

    2e: ^1H NMR ($CDCl_3$), δ: 3.27 (6H, s), 3.85 (6H, s), 4.98 (2H, s), 7.15-7.48 (10H, m) ppm; ^{13}C NMR ($CDCl_3$), δ: 44.44 (d), 52.56 (q), 52.84 (q), 63.37 (s), 127.53, 127.80, and 128.28 (d), 136.60 (s), 167.56 (s), 169.71 (s) ppm.

    3a: ^1H NMR ($CDCl_3$), δ: 1.16 (6H, m), 3.13 (2H, m), 3.72 (12H, s, s) ppm; ^{13}C NMR ($CDCl_3$), δ: 10.80 (q), 36.34 (d), 52.13 (q), 52.74 (q), 61.02 (s), 168.32 (s), 170.79 (s) ppm.

    3b: ^1H NMR ($CDCl_3$), δ: 0.94 (6H, t), 1.53-1.86 (4H, m), 2.93 (2H, m), 3.70 and 3.71 (12H, s, s) ppm; ^{13}C NMR ($CDCl_3$), δ:13.40 (q), 18.99 (t), 43.68 (d), 52.19 (q), 53.23 (q), 60.95 (s), 168.58 (s), 171.07 (s) ppm.

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