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Electrochemical Cyclodimerization of Alkylidenemalonates.

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Abstract: Electrolysis of dimethyl alkylidenemalonates $RCH=C(COOMe)_2$ (R=n-Alk, Ph) in an undivided cell in MeOH in the presence of alkali metal halide as mediator, leads to the formation of cyclic dimers, i.e., 3,4-disubstituted 1,1,2,2-cyclobutanetetracarboxylates. The reaction proceeds via the reductive coupling of two substrate molecules at cathode and the cyclization of a hydrodimer dianion by its interaction with an active form of a mediator, an anode-generated halogen.

Conjugated olefins with electron-withdrawing groups undergo the cyclization at UV light irradiation to afford substituted cyclobutanes[1-3]. These reactions are slow (7-10 days) and low yields are usual for the resulting cyclodimerization products. In the case of cinnamic acid when solid compound is irradiated the yields are high 70-80%, but reaction time is also long (15 days)[4].

Electrocatalytic cyclodimerization of aryl vinyl sulfones in cathodic department of a cell with the formation of a cyclobutane structure[5] is also known. This reaction is distinctly different from well-known processes of activated olefins linear cathodic hydrodimerization[6], and it is hardly applicable for the cyclodimerization of activated olefins of other types.

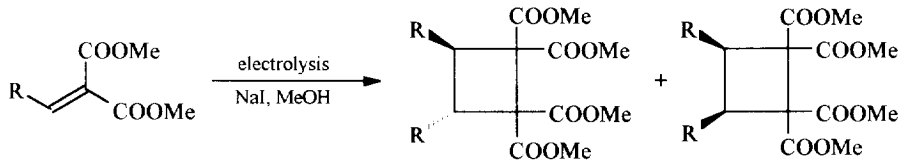
Chemical two-step syntheses of 3,4-dimethylcyclobutane-1,1,2,2-tetracarboxylate[7] and 3,4-diphenylcyclobutane-1,1,2,2-tetracarboxylate[8] from ethylidenemalonate and benzylidenemalonate have been reported. The starting alkylidenemalonate has been reduced with an aluminium amalgam to give 2,3-disubstituted 1,1,4,4-butanetetracarboxylate (5 - 45% yield), the latter has been then cyclized by following treatment with sodium and bromine. Neither a yield at the second stage, nor an isomeric composition of cyclization products has been reported[8].

The other routes to unsubstituted cyclobutanetetracarboxylates are chemical[9] and electrochemical[10,11] cyclization of butane 1,1,4,4-tetracarboxylate in 35-97% yield or electrochemical reaction of 1,2-dibromopropane with ethylenetetracarboxylate in 40% yield[12].

Recently in the course of our study on the electrochemical oxidation of organic compounds in the presence of alkali metal halides[13-16], we have carried out the electrochemical cyclodimerization of alkylidenemalonates with using a new of cyclodimerization concept based on usefulness of both cathodic and anodic electrochemical reactions for the construction of a four-membered ring in an undivided cell[17]. This paper is concerned with the detailed study of this reaction in order to estimate its scope and limitation.

Electrolysis of alkylidenemalonates **1a-e** in methanol was carried out in an undivided cell with Pt anode and glassy carbon cathode in the presence of mediator - NaI or NaBr, at constant current density.

Under these conditions 3,4-disubstituted 1,1,2,2-cyclobutanetetracarboxylates **2a-e** and **3a-e** are formed in 50-70% overall yield (Table 1):



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.

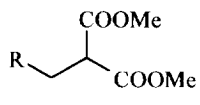
Yields of cyclobutanes **2a-d** and **3a-d** decreased with increasing alkyl chain length of substituent R (Table 1, expts. 1-4).

The yields of trans-isomers **2a-e** were more than those of cis-isomer **3a-e** in every experiment. The ratio of the yields of **2a-d** and **3a-d** was not more than 4:3 when R was alkyl substituents, while R=Ph (**2e** and **3e**) this ratio amounted to 3:1 (Table 1, expt. 5).

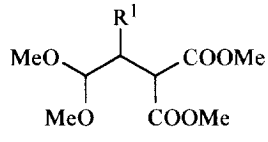
Side products of the reaction were alkylmalonates **4a-e** and 2-alkyl-3,3-dimethoxypropane-1,1-dicarboxylates **5a-d**. The latters are the products of an oxidative rearrangement of alkylidenemalonates, which had been already reported[18].

The methoxylated derivatives of alkylmalonates **6a,b** were formed in some experiments. 2,3-dimethyl-1,1,4,4-butanetetracarboxylate **7a** has been isolated along with **2a** and **3a** when quantity of electricity passed has been decreased (Table 1, expt. 12).

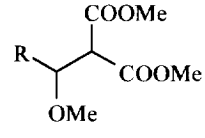
Using acetonitrile as a solvent resulted in substantial decrease of the efficiency of **1a** cyclodimerization, as compared to the reaction carried out in methanol (Table 1, expt. 14). In this case cyclopropane tetraester **8** together with a small amount of 1-(cyanomethyl)-ethylmalonate **9** have been formed.



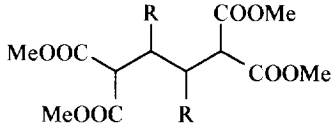
4a R=Me
4b R=Et
4c R=Pr
4d R=C_7H_{15}
4e R=Ph



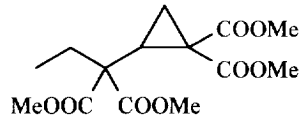
5a R^1=H
5b R^1=Me
5c R^1=Et
5d R^1=C_6H_{13}



6a R=Me
6b R=Ph



7a R=Me
7b R=Ph



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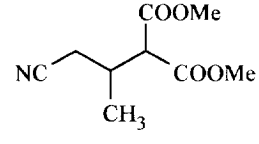

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Table 1. Electrochemical cyclodimerization of alkylidenemalonates **1a-e**[a].

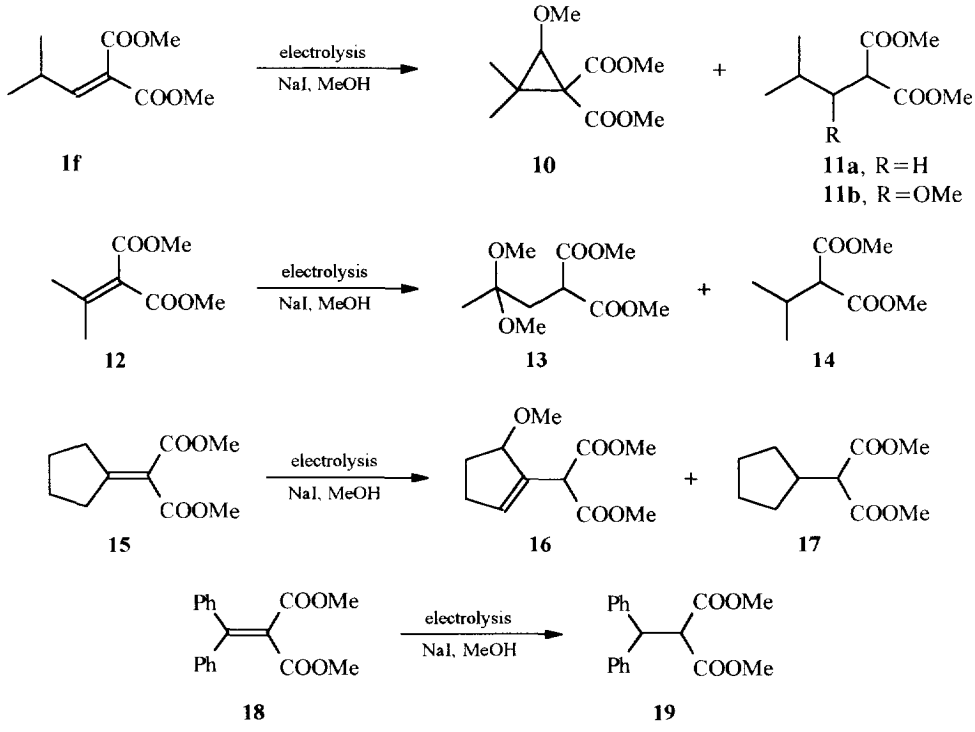
N expt.	Substrate	R	Electricity passed F/mol	Conversion of **1** (%)	Cyclodimers, yield (%)		Other products, yield (%)[b]
					2	**3**	
1	**1a**	Me	7.0	100	42	31	**4a**, 6; **5a**, 10
2	**1b**	Et	5.0	100	39	30	**4b**, 8; **5b**, 12
3	**1c**	Pr	3.7	100	32	26	**4c**, 10; **5c**, 25
4	**1d**	C_7H_{15}	4.0	100	28	24	**4d**, 10; **5d**, 26
5	**1e**	Ph	6.0	93	42	14	**4e**, 17; **6b**, 13
6[c]	**1a**	Me	7.0	100	33	27	**4a**, 8; **5a**, 15; **6a**, 9
7[d]	**1a**	Me	7.0	100	40	30	**4a**, 7; **5a**, 15
8[e]	**1a**	Me	7.0	100	35	23	**4a**, 5; **5a**, 27
9[f]	**1a**	Me	7.0	100	27	22	**4a**, 6; **5a**, 30; **6a**, 8
10[g]	**1a**	Me	7.0	100	31	25	**4a**, 7; **5a**, 32
11[h]	**1a**	Me	7.0	93	8	2	**5a**, 5; **6a**, 19; **7a**, 37
12	**1a**	Me	2.0	100	17	5	**4a**, 5; **5a**, 10; **6a**, 5; **7a**, 50
13[i]	**1a**	Me	5.0	100	19	15	**4a**, 4; **5a**, 49
14[k]	**1a**	Me	2.0	100	16	12	**8**, 46; **9**, 17

[a] 10 mmol of **1a-e**, 7 mmol of NaI in 20 ml MeOH, glassy carbon cathode, Pt anode, electrolysis at 60°C with current density 80 mA/cm^2. [b] Yields listed are based on GLC and ^{1}H NMR data. [c] Mediator: NaBr. [d] Pb cathode. [e] C cathode. [f] Fe cathode. [g] Current density 120 mA/cm^2. [h] Current density 40 mA/cm^2. [i] Temperature 20°C. [k] Solvent: MeCN

We have found that current density and material of cathode effect on the yields of ester **2** and **3** significantly. The replacement of a glassy carbon cathode with lead, graphite or iron one caused a decrease in the cyclodimerization products **2a** and **3a** yields and an increase in the yield of the oxidative rearrangement product, ester **5a** (Table 1, expts 7-9). These differences were the most significant, when Fe cathode has been used. Increasing the current density to 120 mA/cm^2 (Table 1, expt. 10) and decreasing temperature (Table 1, expt. 13) led to the similar results. Under the conditions of electrochemical rearrangement of alkylidenemalonates[18] (Fe cathode, current density of 220 mA/cm^2) cyclodimerization products **2a-c** and **3a-c** have been formed only in 1 - 5% yields.

Reducing the current density to 40 mA/cm^2 also resulted in decreasing the yields of cyclodimers **2a** and **3a**; in this case lowering of **1a** conversion and the formation of methoxy derivative **6a** together with a considerable amount of dimeric ester **7a** were also observed (Table 1, expt. 11).

Under the conditions of electrochemical dimerization of esters **1a-e**, dimethyl isobutylidenemalonate **1f**, as well as alkylidenemalonates with the completely substituted double bond, such as isopropylidenemalonate **12**, cyclopentylidenemalonate **15** and diphenylmethylenemalonate **18** did not afford the substituted 1,1,2,2-cyclobutanetetracarboxylates of types **2** and **3**. In these cases hydrogenation of the double bond and oxidative rearrangement[18] (provided the latter is structurally possible) took place (Table 2).



Electrolysis of methyl benzylideneacetoacetate **20** under the similar conditions led to the formation of only one isomer of cyclopentene derivative **21**. The most probable by steric reasons structure of **21** is shown on reaction scheme:

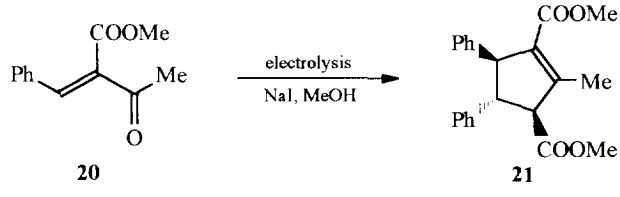


Table 2. Electrolysis of alkylidenemalonates **1f**, **12**, **15**, **18** and benzylideneacetoacetate **20**[a].

Substrate	Electricity passed, F/mol	Conversion, %	Yields of reaction products, % [b]
1f	4.1	90	**10**, 55; **11a**, 21; **11b**, 10
12	2.2	98	**13**, 48; **14**, 39
15	4.0	90	**16**, 48; **17**, 38
18	11.0	66	**19**, 56
20	2.2	100	**21**, 46

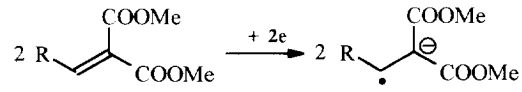
[a] 10 mmol of substrate, 7 mmol of NaI in 20 ml of MeOH, glassy carbon cathode, Pt anode, electrolysis at 60°C, 80 mA/cm^2.

[b] Yields on substrate taken.

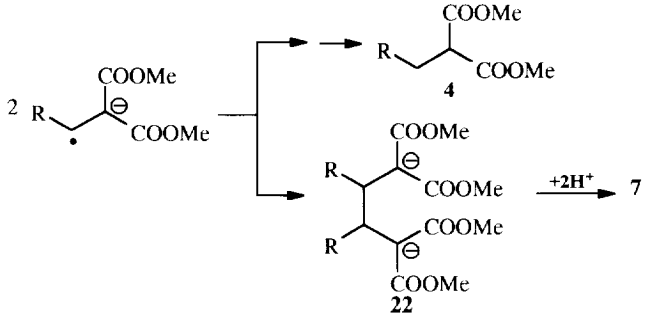
Mechanism of electrochemical cyclodimerization of alkylidenemalonates **1a-e** consists in the reduction of **1** at cathode with the following coupling of two anion-radicals and cyclization of resulting dianion **22** in solution under the action of an anodically generated halogen with the regeneration of a mediator - halogenide anion:

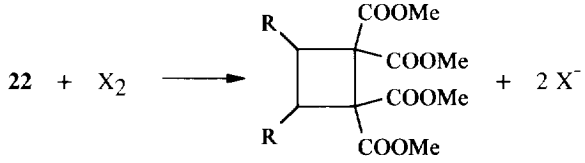
at anode: $2X^- - 2e \longrightarrow X_2$ (X=I, Br)

at cathode:



in solution:





Besides the coupling of the two olefinic molecules, the cathodic reduction leads to the formation of the products of the double bond hydrogenation, *i.e.*, the esters of type **4**. The correlation between these two processes depends on the structure of initial olefin molecule. For substrates with bulky R substituents and completely substituted olefins the dimerization becomes suppressed for steric reasons and the hydrogenation and other side reactions take place.

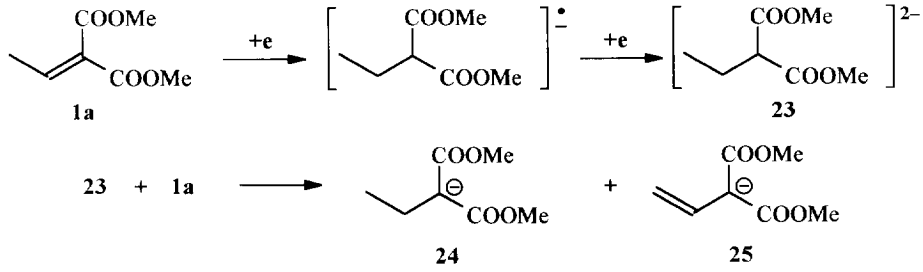
Protonation of dianion **22** in methanol leads to a hydrodimer **7** that has been isolated when the electrolysis of **1a** had been stopped at an intermediate stage (expt. 12, Table 1). In order to complete the cyclodimerization, a rather great amount of electricity (4 - 7 F/mol) should be passed, so the interaction of dianion **22** with a molecular halogen is the slowest stage of the process under the conditions studied. Hence, hydrodimer **7** accumulates in the system and then undergoes the slow cyclization into esters **2** and **3**, according to the mechanism that we have earlier proposed for cyclization of 1,1,3,3-propanetetracarboxylates[14]. The cathodic reduction of anodically generated halogen and halogen catalysed oxidation of methoxide-anion[10] are the side reactions, which reduce the efficiency of the whole process.

Linear hydrodimer **7a** was formed as a mixture of nearly equal amounts of *meso*- and *dl*-isomers (NMR data), which were isolated and characterised by physico-chemical methods. The ratio of the yields of **2** and **3** with *trans*- and *cis*-configuration of substituents R depends on cyclization rates of *dl*- and *meso*-

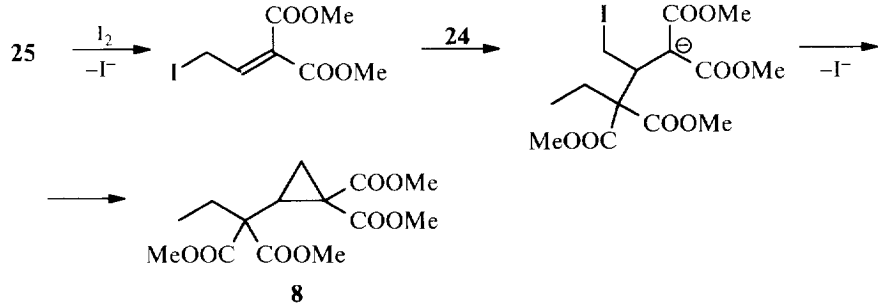
forms. The cyclization of *meso*-form proceeds slowly due to the unfavourable *cis*-position of substituents R in resulting cyclobutane derivative **3**.

In a special experiment *meso*-**7b** and *dl*-**7b** have been isolated in 35 and 32% yields respectively at electrolysis of **1e** (R=Ph) using $NaClO_4$ as an electrolyte instead of NaI. Having been electrolysed in the presence of NaI, *dl*-**7b** was transformed into **2e** in 75% yield, while *meso*-**7b** afforded **3e** only in 25% yield under the same conditions.

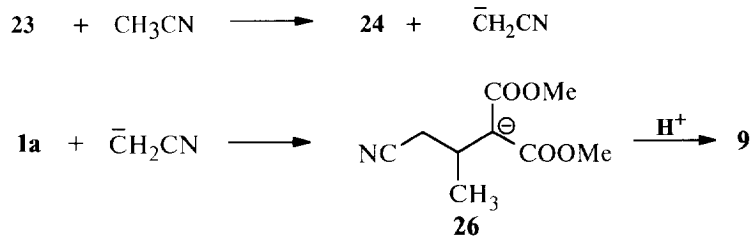
The further reduction of initially formed anion-radicals predominated over their recombination into dimeric dianion when acetonitrile was used as a solvent for the electrolysis of dimethyl ethylidenemalonate **1a**. In an aprotic solvent dianion **23** just formed abstracts a proton from substrate **1a**, leading to formation of two anions, **24** and **25**:



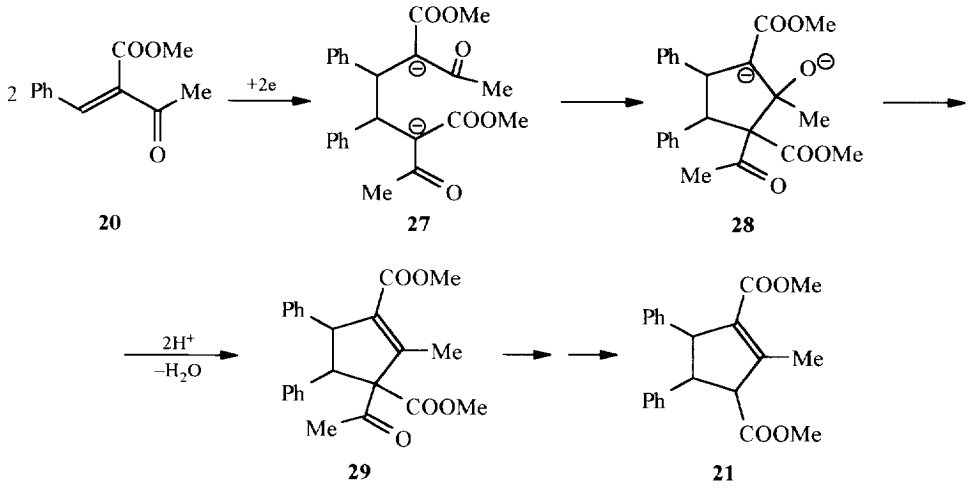
Further interaction of anion **25** with anode-generated molecular iodine to afford cyclopropane tetraester **8** proceeds according to the scheme approximating the one described earlier for an oxidative rearrangement of alkylidenemalonates[18].



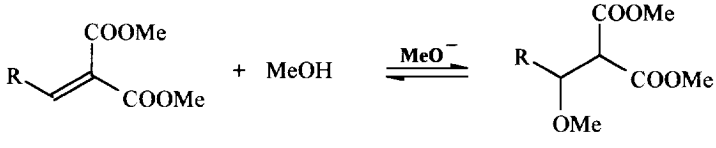
An abstraction of a proton from acetonitrile by dianion **23** occurs in a less extent. The resulting cyanomethylide adds to ethylidenemalonate to afford anion **26**, the latter is protonated into compound **9**:



When benzylideneacetoacetate **20** reduced at cathode, the resulting cyclic dianion **28**, have been transformed into β-keto ester **29** which underwent further the ketone cleavage under the reaction condition to give ester **21**:



The best yields of cyclodimers **2** and **3** have been achieved using a glassy carbon cathode at current density of 80 mA/cm^2. Among other cathode materials studied, the best results have been obtained using cathodes with high hydrogen overvoltage. Increasing the current density results in increasing side reactions, *i.e.*, cathodic reduction of solvent and electrolyte. Both these reactions lead to hydrogen evolution and to methoxide-anions formation. These conditions are more favourable for the oxidative rearrangement of alkylidenemalonates[18]. A decrease of a cathodic current density results in a decrease of efficiency of the process as a whole. Under these conditions the formation of ester **6** (the product of catalysed by electrogenerated base addition of methanol to the activated double bond of **1**) was observed and an incomplete conversion of a substrate took place. The **6** formation is reversible reaction and under conditions, when the substrate reacts more efficiently, the balance is moved to the left:



Structures of **2a** and **2e** were confirmed by X-ray crystallographic analysis (Fig. 1 and Fig. 2). The assignment of other 3,4-dialkyl substituted 1,1,2,2-cyclobutanetetracarboxylates based on the analysis of their NMR spectra in comparison with those of the established structures **2a** and **3a** (Table 3). In the ^{1}H NMR spectra of structures **3a-d** with *cis*-positioned alkyl substituents the signals for the protons of cyclobutane CH-fragments are moved downfield by 0.18 - 0.28 ppm comparatively to the signals for the same protons in structures **2a-d** with the *trans*-positioned alkyl substituents. In the ^{13}C NMR spectra the

signals for the carbon atoms of the same fragments of structures **3a-d** are moved upfield by 1.7 - 3.3 ppm relatively to the analogous signals of structures **2a-d**.

Table 3. Signals of CH-groups for *trans*- and *cis*-dialkylsubstituted cyclobutane-1,1,2,2-tetracarboxylates **2a-d** and **3a-d**.

R	^{1}H NMR ($CDCl_3$), δ, ppm.				Δδ	^{13}C NMR ($CDCl_3$), δ, ppm.				Δδ
CH_3	2.85	**(2a)**	3.13	**(3a)**	0.28	39.7	**(2a)**	36.3	**(3a)**	3.4
C_2H_5	2.74	**(2b)**	2.93	**(3b)**	0.19	45.4	**(2b)**	43.7	**(3b)**	1.7
C_3H_7	2.81	**(2c)**	2.99	**(3c)**	0.18	43.5	**(2c)**	41.6	**(3c)**	1.9
$CH_3(CH_2)_6$	2.81	**(2d)**	2.99	**(3d)**	0.18	43.4	**(2d)**	41.6	**(3d)**	1.8

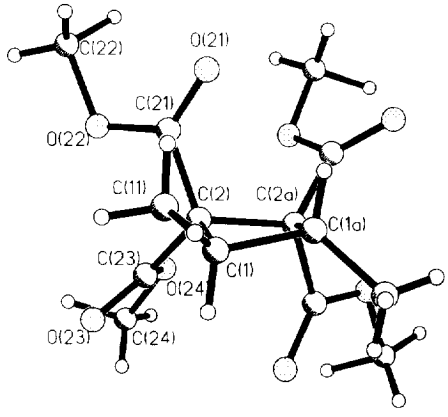


Fig. 1 General view of a molecule of tetramethyl *trans*-3,4-dimethylcyclobutane-1,1,2,2-tetracarboxylate **2a**

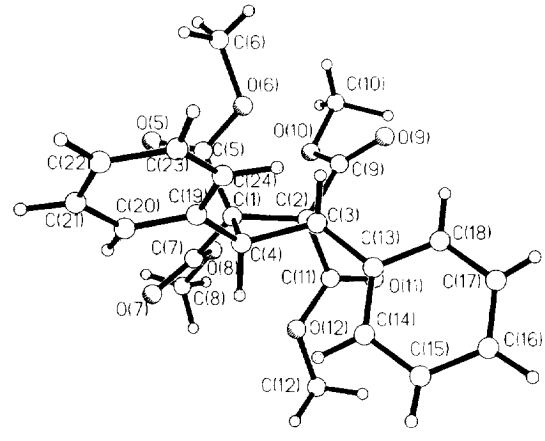


Fig. 2 General view of a molecule of tetramethyl *trans*-3,4-diphenylcyclobutane-1,1,2,2-tetracarboxylate **2e**

EXPERIMENTAL PART

GLC analyses were performed on a LKhM-80 chromatograph fitted with a flame-ionisation detector. Glass columns used were 1000x3mm (5% OV-17 on Inerton, 0.16-0.20mm) and 3000×3mm (1% SE-54 on AW Inerton, 0.16-0.20mm).

^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz) or Bruker AM-300 (300 MHz) spectrometer in $CDCl_3$. The chemical shifts are presented in δ scale with TMS used as internal standard.

X-ray analysis. Intensities of reflection were measured on an automatic four-circled Hilger Watts Y-290 diffractometer (MoK_α graphite-monochromator; $\Theta/2\Theta$ scan, $\Theta_{max}=22°$) or an Syntex $P2_1$ diffractometer (MoK_α graphite-monochromator; $\Theta/2\Theta$ scan, $\Theta_{max}=30°$).

Dimethyl alkylidenemalonates and methyl benzylideneacetoacetate were prepared by the condensation of dimethyl malonate or methyl acetoacetate with the corresponding aldehydes and ketones according to literature methods[19].

Electrochemical cyclodimerization of alkylidenemalonates. General procedure. A solution of alkylidenemalonate **1** (10 mmol), NaI or NaBr (7 mmol) in 20 ml of methanol in undivided cell equipped with external cooling, a glassy carbon cathode, platinum anode, a magnetic stirrer and thermometer was electrolysed under the constant current at 60°C until the quantities of the electricity indicated in Tables 1 and 2 were passed. The substrates conversions and the yields of esters **4a-e** and **7a,b** were determined by GLC analysis. The reaction mixture was concentrated. The residue was extracted with $CHCl_3$. The extract was washed with an aqueous solution of $Na_2S_2O_3$. The organic layer was separated, dried over Na_2SO_4, concentrated and analysed quantitatively using the NMR spectroscopy with 1,4-dichlorobenzene as an internal standard. Electrolysis products were isolated by crystallisation or column chromatography (with ether/hexane 1:2 mixture as the eluent). The reaction products were eluted in the order: alkylmalonates **4**, methoxysubstituted alkylmalonates **6**, rearrangement products **5**, *cis*-cyclodimers **3**, trans-cyclodimers **2**.

Tetramethyl *trans*-3,4-dimethylcyclobutane-1,1,2,2-tetracarboxylate (2a), was isolated in 31% yield by crystallisation of the reaction mixture obtained in expt. 1 (Table 1) from MeOH; m.p. 155-157°C (in a sealed capillar); ^{1}H NMR (δ, ppm): 1.00 m (6H, CH_3), 2.85 m (2H, CH), 3.71 s and 3.73 s (12H, $COOCH_3$). ^{13}C NMR (δ, ppm): 14.41 q (CH_3), 39.71 d (CH), 52.32 q and 52.50 q (OCH_3), 61.82 s (C^{tert}), 168.42 s and 169.64 s (C=O). Anal. Calcd for $C_{14}H_{20}O_8$: C 53.16; H 6.33. Found: C 53.34; H 6.51.

Tetramethyl *cis*-3,4-dimethylcyclobutane-1,1,2,2-tetracarboxylate (3a), was isolated in 25% yield by column chromatography (ether/hexane 1:1 as an eluent) of the reaction mixture obtained in expt. 1 (Table 1); n_D^{24} 1.4651; ^{1}H NMR (δ, ppm): 1.16 m (6H, CH_3), 3.13 m (2H, CH), 3.72 s (12H, $COOCH_3$). ^{13}C NMR (δ, ppm): 10.80 q (CH_3), 36.34 d (CH), 52.13 q and 52.74 q (OCH_3), 61.02 s (C^{tert}), 168.32 s and 170.79 s (C=O).

Tetramethyl *trans*-3,4-diethylcyclobutane-1,1,2,2-tetracarboxylate (2b), was isolated in 30% yield by crystallisation of the reaction mixture obtained in expt. 2 (Table 1) from MeOH; m.p. 112-113°C; ^{1}H NMR (δ, ppm): 0.92 t (6H, CH_3), 1.40 m (4H, CH_2), 2.74 m (2H, CH), 3.71 s and 3.73 s (12H, $COOCH_3$). ^{13}C NMR (δ, ppm): 11.96 q (CH_3), 24.74 t (CH_2), 45.40 d (CH), 52.36 q and 52.51 q (OCH_3), 56.41 s (C^{tert}), 168.74 s and 169.91 s (C=O). Anal. Calcd for $C_{16}H_{24}O_8$: C 55.61; H 6.96. Found: C 55.69; H 6.69.

Tetramethyl *cis*-3,4-diethylcyclobutane-1,1,2,2-tetracarboxylate (3b), was isolated in 18% yield from the reaction mixture obtained in expt. 2 (Table 1) by column chromatography (ether/hexane 1:2 as an eluent); m.p. 74-75°C; ^{1}H NMR (δ, ppm): 0.94 t (6H, CH_3), 1.53-1.86 m (4H, CH_2), 2.93 m (2H, CH), 3.70 s and 3.71 s (12H, $COOCH_3$). ^{13}C NMR (δ, ppm): 13.40 q (CH_3), 18.99 t (CH_2), 43.68 d (CH), 52.19 q and 53.23 q (OCH_3), 60.95 s (C^{tert}), 168.58 s and 171.07 s (C=O).

Tetramethyl *trans*-3,4-dipropylcyclobutane-1,1,2,2-tetracarboxylate (2c) and **tetramethyl *cis*-3,4-dipropylcyclobutane-1,1,2,2-tetracarboxylate (3c)**. Column chromatography (ether/hexane 1:1 as an eluent) of the reaction mixture from expt. 3 (Table 1) yielded 48% of a mixture of **2c** and **3c** in 29:21 ratio; n_D^{25} 1.4641; ^{1}H NMR (δ, ppm): 0.87 t and 0.89 t (6H, CH_3), 1.19-1.82 m (8H, CH_2), 2.81 m and 2.99 m (2H, CH), 3.70 s, 3.71 s and 3.72 s (12H, $COOCH_3$). ^{13}C NMR (δ, ppm): 14.19 q and 14.20 q (CH_3), 20.50 t, 21.96 t, 28.14 t, 33.99 t (CH_2), 41.66 d and 43.45 d (CH), 52.16 q, 52.31 q, 52.47 q and 52.79 q (OCH_3), 60.99 s and 61.64 s (C^{tert}), 168.64 s, 168.76 s, 169.63 s and 171.10 s (C=O). Anal. Calcd for $C_{18}H_{26}O_8$: C 58.15; H 7.72. Found: C 58.06; H 7.53.

Tetramethyl *trans*-3,4-diheptylcyclobutane-1,1,2,2-tetracarboxylate (2d) and **tetramethyl *cis*-3,4-diheptylcyclobutane-1,1,2,2-tetracarboxylate (3d)**. Column chromatography (ether/hexane 1:1 as an eluent) of the reaction mixture from expt. 4 (Table 1) yielded 42% of a mixture of **2d** and **3d** in 27:23 ratio; as viscous oil; ^{1}H NMR (δ, ppm): 0.88 t and 0.89 t (6H, CH_3), 1.12-1.82 m (24H, CH_2), 2.81 m and 2.99 m (2H, CH), 3.71 s, 3.72 s, 3.73 s and 3.74 s (12H, $COOCH_3$). ^{13}C NMR (δ, ppm): 13.51 q and 13.72 q (CH_3), 22.21 t, 22.31 t, 25.68 t, 26.94 t, 28.56 t, 28.87 t, 29.14 t, 29.52 t, 31.24 t and

31.46 t (CH_2), 41.63 d and 43.44 d (CH), 51.86 q, 52.18 q, 52.46 q and 52.65 q (OCH_3), 60.76 s and 61.42 s (C^{tert}), 168.34 s, 168.53 s, 169.64 s and 170.83 s (C=O). Anal. Calcd for $C_{26}H_{44}O_8$: C 64.25; H 9.02. Found: C 64.46; H 9.09.

Tetramethyl *trans*-3,4-diphenylcyclobutane-1,1,2,2-tetracarboxylate (2e), was isolated in 35% yield by crystallisation from the reaction mixture expt. 5 (Table 1); m.p. 151-152°C (ether/hexane). ^1H NMR (δ, ppm): 3.27 s and 3.85 s (12H, $COOCH_3$), 4.98 s (2H, CH), 7.15-7.48 m (10H, C_6H_5). ^{13}C NMR (δ, ppm): 44.44 d (CH), 52.46 q and 52.84 q (OCH_3), 63.37 s (C^{tert}), 127.53 d, 127.80 d, 128.28 d and 136.60 s (C_6H_5), 167.56 s and 169.71 s (C=O). Anal. Calcd for $C_{24}H_{24}O_8$: C 65.45; H 5.45. Found: C 66.04; H 5.61.

Tetramethyl *cis*-3,4-diphenylcyclobutane-1,1,2,2-tetracarboxylate (3e), was prepared by electrochemical cyclization of tetramethyl *meso*-2,3-diphenylbutane-1,1,4,4-tetracarboxylate **7b** in the presence of NaI. Column chromatography (ether/hexane 1:1 as an eluent) afforded of **3e** 15% as a viscous oil: ^1H NMR (δ, ppm): 3.56 s and 3.85 s (12H, $COOCH_3$), 4.92 s (2H, CH), 7.14 m (10H, C_6H_5). ^{13}C NMR (δ, ppm): 47.34 d (CH), 52.38 q and 53.41 q (OCH_3), 62.51 s (C^{tert}), 126.59 d, 127.41 d, 130.05 d and 135.91 s (C_6H_5), 167.75 s and 171.37 s (C=O).

Dimethyl 3,3-dimethoxypropane-1,1-dicarboxylate (5a), n_D^{27} 1.4290; b.p. 67-68°C (0.03 Torr). ^1H NMR (δ, ppm): 2.19 dd (2H, CH_2, J_1=7.2 Hz, J_2=5.4 Hz), 3.29 s (6H, OCH_3), 3.50 t (1H, **CH**$(COOCH_3)_2$, J=7.2 Hz), 3.71 s (6H, OCH_3), 4.38 t (1H, **CH**$(OCH_3)_2$, J=5.4 Hz). ^{13}C NMR (δ, ppm): 31.6 t (CH_2), 47.1 d [**CH**$(COOCH_3)_2$], 52.1 q and 53.1 q (OCH_3), 102.3 d [**CH**$(OCH_3)_2$], 169.2 s (C=O). Anal. Calcd for $C_9H_{16}O_6$: C 49.09; H 7.27. Found: C 48.78; H 7.23.

Dimethyl 2-methyl-3,3-dimethoxypropane-1,1-dicarboxylate (5b), n_D^{27} 1.4334; b.p. 125-127°C (10 Torr). ^1H NMR (δ, ppm): 0.98 d (3H, CH_3), 2.55 m (1H, **CH**-CH_3), 3.31 s and 3.33 s (6H, OCH_3), 3.50 d (1H, **CH**$(COOCH_3)_2$), 3.70 s (6H, OCH_3), 4.26 d (1H, **CH**$(OCH_3)_2$). ^{13}C NMR (δ, ppm): 12.1 q (CH_3), 36.4 d (CH), 52.1 q, 52.2 q, 53.7 q and 55.2 q (OCH_3), 52.9 d [**CH**$(COOCH_3)_2$], 106.4 d [**CH**$(OCH_3)_2$], 169.0 s and 169.3 s (C=O).

Dimethyl 2-ethyl-3,3-dimethoxypropane-1,1-dicarboxylate (5c), n_D^{27} 1.4383; b.p. 71-72°C (0.04 Torr). ^1H NMR (δ, ppm): 0.90 t (3H, CH_3), 1.28-1.68 m (2H, CH_2), 2.40 m (1H, **CH**-CH_2), 3.30 s and 3.35 s (6H, OCH_3), 3.57 d (1H, **CH**$(COOCH_3)_2$), 3.68 s (6H, OCH_3), 4.40 d (1H, **CH**$(OCH_3)_2$). ^{13}C NMR (δ, ppm): 11.6 q (CH_3), 20.5 t (CH_2), 42.9 d and 51.0 d (CH), 51.9 q, 53.6 q, and 55.5 q (OCH_3), 105.8 d [**CH**$(OCH_3)_2$], 169.1 s and 169.3 s (C=O).

Dimethyl 2-(2,2-dimethoxyethyl)octane-1,1-dicarboxylate (5d), b.p. 82-84°C (0.03 Torr). ^1H NMR (δ, ppm): 0.88 t (3H, CH_3), 1.15-1.74 m (10H, CH_2), 2.38 m (1H, CH), 3.31 s and 3.36 s (6H, OCH_3), 3.55 d (1H, **CH**$(COOCH_3)_2$), 3.66 s (6H, OCH_3), 4.44 d (1H, **CH**$(OCH_3)_2$).

Dimethyl α-methoxyethylmalonate (6a) was prepared by addition of MeOH to dimethyl ethylidenemalonate in the presence of MeONa (0.2 equiv.), n_D^{23} 1.4334, b.p. 88-90° (0.04 Torr). ^1H NMR (δ, ppm): 1.22 d (3H, CH_3), 3.31 s (3H, OCH_3), 3.47 d (1H, CH), 3.82 s and 3.84 s (6H, OCH_3), 3.89 m (1H, CH). ^{13}C NMR (δ, ppm): 16.9 q (CH_3), 52.5 q and 56.9 q (OCH_3), 58.1 d (**CH**$(COOCH_3)_2$), 75.4 d (**CH**OCH_3), 167.6 s and 168.0 s (C=O).

Dimethyl α-methoxybenzylmalonate (6b) was prepared by addition of MeOH to dimethyl benzylidenemalonate in the presence of MeONa (0.2 equiv.). Column chromatography afforded **6b** (62%); n_D^{24} 1.4965. ^1H NMR (δ, ppm): 3.19 s, 3.48 s and 3.80 s (9H, OCH_3), 3.82 d (1H, **CH**$(COOCH_3)_2$, J=9.5 Hz), 4.81 d (1H, C**H**OCH_3, J=9.5 Hz), 7.20-7.43 m (5H, C_6H_5). ^{13}C NMR (δ, ppm): 52.05 q and 56.27 q (OCH_3), 59.28 d [**CH**$(COOCH_3)_2$], 81.35 d (**CH**OCH_3), 127.24 d, 128.01 d, 128.47 d and 137.50 s (C_6H_5), 166.02 s and 167.06 s (C=O).

Tetramethyl *meso*-2,3-dimethylbutane-1,1,4,4-tetracarboxylate (7a), was isolated in 25% yield by crystallisation of the reaction mixture from expt. 12 (Table 1); m.p. 104-105°C (ether/hexane). ^1H NMR (δ, ppm): 1.02 d (6H, CH_3), 2.34 m (2H, **CH**-CH_3), 3.48 d (2H, **CH**$(COOCH_3)_2$, J=6.4 Hz),

3.70 s and 3.71 s (12H, OCH_3). ^{13}C NMR (δ, ppm): 14.59 q (CH_3), 36.63 d (**CH**-CH_3), 52.25 q and 52.52 q (OCH_3), 53.69 d [**CH**($COOCH_3$)$_2$], 168.87 s and 169.39 s (C=O).

Tetramethyl *dl*-2,3-dimethylbutane-1,1,4,4-tetracarboxylate (7a), was isolated in 10% yield by crystallisation of the reaction mixture from expt. 12 (Table 1); m.p. 61-62°C (ether/hexane). ^1H NMR (δ, ppm): 0.83 d (6H, CH_3), 2.32 m (2H, **CH**-CH_3), 3.32 d (2H, **CH**($COOCH_3$)$_2$, J=9.6 Hz), 3.69 s and 3.73 s (12H, OCH_3). ^{13}C NMR (δ, ppm): 11.21 q (CH_3), 34.66 d (**CH**-CH_3), 52.26 q and 52.44 q (OCH_3), 56.10 d [**CH**($COOCH_3$)$_2$], 168.26 s and 168.55 s (C=O).

Dimethyl (1,1-dimethoxycarbonylpropyl)-cyclopropane-1,1-dicarboxylate (8), was isolated in 12% yield by column chromatography (ether/hexane 2:1 as eluent); m.p. 83-85°C. ^1H NMR (δ, ppm): 0.92 t (3H, CH_3), 1.51 dd (1H, C**H$_a$**H$_b$-CH$_c$, $^2J_{H_aH_b}$=-5.3 Hz, $^3J_{H_aH_c}$=10.2 Hz), 1.81 dd (1H, CH$_a$**H$_b$**-CH$_c$, $^2J_{H_aH_b}$=-5.3 Hz, $^3J_{H_bH_c}$=8.9 Hz), 2.01 q (2H, **CH$_2$**-CH_3), 2.51 dd (1H, CH$_a$H$_b$-C**H$_c$**, $^3J_{H_cH_a}$=10.2 Hz, $^3J_{H_cH_b}$=8.9 Hz), 3.68 s, 3.71 s and 3.73 s (12H, OCH_3). ^{13}C NMR (δ, ppm): 8.96 q (CH_3), 18.44 t (CH_2), 27.94 t (CH_2), 29.76 d (CH), 32.76 s (C^{tert}), 52.26 q and 52.42 q (OCH_3), 57.14 s (C^{tert}), 167.97 s, 168.32 s, 169.56 s and 170.23 s (C=O). Anal. Calcd for $C_{14}H_{20}O_8$: C 53.16; H 6.13. Found: C 52.94; H 6.38.

Dimethyl 2-methyl-3-cyanopropane-1,1-dicarboxylate (9), was isolated in 38% yield by column chromatography (ether/hexane 1:1 as eluent). ^1H NMR (δ, ppm): 1.12 d (3H, CH_3), 1.35 m and 2.53 m (2H, CH_2), 2.55 m (1H, CH), 3.37 d (1H, CH), 3.79 s (6H, OCH_3). ^{13}C NMR (δ, ppm): 17.3 q (CH_3), 22.1 t (CH_2), 30.4 d (CH), 52.7 q (OCH_3), 55.2 d (CH), 117.9 s (CN), 168.1 s (C=O).

Dimethyl 2-methoxy-3,3-dimethylcyclopropane-1,1-dicarboxylate (10), was prepared in 61% yield by distillation *in vacuo* of the residue obtained after the standard workup of the reaction mixture; b.p. 48-49°C (0.04 Torr); n_D^{27} 1.4444. ^1H NMR (δ, ppm): 1.19 s and 1.30 s (6H, CH_3), 3.48 s (3H, OCH_3), 3.63 s (1H, CH), 3.70 s and 3.73 s (6H, OCH_3). ^{13}C NMR (δ, ppm): 16.6 q and 19.6 q (CH_3), 31.7 s and 41.9 s (C^{tert}), 52.2 q, 52.3 q and 58.7 q (OCH_3), 72.2 d (**CH**OCH_3), 166.1 s and 168.5 s (C=O). Anal. Calcd for $C_{10}H_{16}O_5$: C 55.55; H 7.41. Found: C 53.86; H 7.49.

Dimethyl 3-methyl-2-methoxybutane-1,1-dicarboxylate (11b), was prepared by addition of MeOH to dimethyl isopropylidenemalonate in the presence of MeONa (0.2 equiv.), n_D^{23} 1.4328; b.p. 56-57°C (0.04 Torr). ^1H NMR (C_6D_6, δ, ppm): 0.89 d (6H, CH_3), 1.84 m (1H, CH), 3.26 s 3.32 s and 3.34 s (9H, OCH_3), 3.79 d (1H, CH), 3.91 dd (1H, C**H**OCH_3). ^{13}C NMR (δ, ppm): 16.2 q (CH_3), 31.2 d (CH), 52.2 q, 52.3 q and 55.4 q (OCH_3), 60.9 d (CH), 84.3 d (**CH**OCH_3), 167.9 s (C=O).

Dimethyl 3,3-dimethoxybutane-1,1-dicarboxylate (13); n_D^{22} 1.4365; b.p. 90-92°C (0.1 Torr). ^1H NMR (δ, ppm): 1.21 s (1H, CH_3), 2.27 d (2H, CH_2), 3.15 s (6H, OCH_3), 3.47 t (1H, CH), 3.71 s (6H, OCH_3). ^{13}C NMR (δ, ppm): 20.6 q (CH_3), 35.4 t (CH_2), and 47.7 d (CH), 48.9 q and 52.4 q (OCH_3), 102.2 d [**CH**(OCH_3)$_2$], 169.8 s (C=O).

Dimethyl (5-methoxypent-1-enyl)-malonate (16), was isolated by column chromatography (ether/hexane 2:1 as the eluent) of the reaction mixture; n_D^{27} 1.4706. ^1H NMR (δ, ppm): 1.72 m and 2.05-2.30 m (4H, CH_2), 3.24 s (3H, OCH_3), 3.72 s and 3.74 s (6H, OCH_3), 4.29 s (1H, **CH**($COOCH_3$)$_2$), 4.42-4.51 m (1H, **CH**OCH_3), 5.96 m (1H, CH=). ^{13}C NMR (δ, ppm): 28.8 t and 30.2 t (CH_2), 50.7 d [**CH**($COOCH_3$)$_2$], 52.3 q, 52.4 q and 55.7 q (OCH_3), 86.1 d (**CH**OCH_3), 133.7 d (CH=), 135.6 s (C=), 168.1 s and 168.3 s (C=O). Anal. Calcd for $C_{11}H_{16}O_5$: C 57.89; H 7.02. Found: C 57.72; H 7.00.

Dimethyl 2-methyl-4,5-diphenylcyclopent-1-ene-1,3-dicarboxylate (21) was prepared *via* electrochemical cyclodimerization of methyl benzylideneacetoacetate **20** by general procedure in the presence of NaI (2.2 F/mol of electricity passed). Column chromatography afforded **21** (50%); m.p. 136-139°C (MeOH). ^1H NMR (δ, ppm): 2.35 m (3H, CH_3), 3.62 s and 3.68 s (6H, OCH_3), 4.12 d (1H, CH), 4.22 t (1H, CH), 4.48 d (1H, CH), 6.68-6.86 m and 7.00-7.10 m (4H + 6H, 2xC_6H_5). ^{13}C NMR (δ, ppm): 14.70 q (CH_3), 51.15 q and 52.07 q (OCH_3), 52.89 d, 56.01 d, and 58.96 d (CH), 126.37 d, 124.48 d 127.66 d, 127.78 d, 128.05 d, 128.15 d, 128.61 d, 137.75 s, 138.76 s (2xC_6H_5 and CH=), 152.66 c

(C=), 165.30 s (=C-C=O), 172.87 s (C=O). Anal. Calcd for $C_{22}H_{22}O_4$: C 75.43; H 6.29. Found: C 75.28; H 6.38.

Electrochemical synthesis of tetramethyl 2,3-diphenylbutane-1,1,4,4-tetracarboxylate (7b) and the following cyclization of the diastereomers of ester (7b) thus obtained. The solution of the dimethyl benzylidenemalonate **1f** (18 mmol) in methanol was electrolysed by standard procedure using $NaClO_4$ (9 mmol) as an electrolyte and passing 4.0 F/mol of electricity. Fractional crystallisation from methanol of the reaction mixture obtained provided: **tetramethyl *meso*-2,3-diphenylbutane-1,1,4,4-tetracarboxylate (7b)** (35%), m.p. 164-166°C; ^{1}H NMR (δ, ppm): 3.37 s and 3.43 s (12H, OCH_3), 3.68 d and 3.71 d (2H, CH), 4.11 dd (2H, CH), 7.22-7.35 m (10H, C_6H_5); ^{13}C NMR (δ, ppm): 48.57 d (CH), 52.23 q and 53.07 q (OCH_3), 55.66 d (CH), 127.59 d, 128.12 d, 129.90 d and 137.91 s (C_6H_5), 167.95 s and 168.54 s (C=O) and **tetramethyl *dl*-2,3-diphenylbutane-1,1,4,4-tetracarboxylate (7b)** (32%), m.p. 138-141°C; ^{1}H NMR (δ, ppm): 3.30 s (6H, OCH_3), 3.82 s (4H, CH), 3.94 s (6H, OCH_3), 6.60-7.30 m (10H, C_6H_5); ^{13}C NMR (δ, ppm): 46.60 d (CH), 52.23 q and 53.07 q (OCH_3), 55.20 d (CH), 127.47 d, 127.86 d, 130.08 d, 135.52 s (C_6H_5), 167.54 s and 168.29 s (C=O).

Electrochemical cyclization of *meso*-**7b** was carried out according to the standard procedure for cyclodimerization of alkylidenemalonates in the presence of NaI by passing 2.0 F/mol of electricity. The yield of **3e** was 25% on substrate taken (48% of conversion). *dl*-**7b** under the same conditions afforded ester **2e** in 75% yield (80% of conversion).

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