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Tetrahedron
Tetrahedron 62 (2006) 3989–3996

Stereoselective electrocatalytic transformation of malonate and alkylidenecyanoacetates into (*E*)-3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylates

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Received 10 November 2005; revised 19 January 2006; accepted 10 February 2006

Available online 9 March 2006

Abstract—Electrolysis of malonate and alkylidenecyanoacetates in alcohols in an undivided cell in the presence of NaBr results in stereoselective formation of (*E*)-3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylates in 75–90% yields.

1. Introduction

Functionalized cyclopropanes possess a wide spectrum of physiological activities[1] and belong to an important class of compounds used in the synthesis of natural biologically active substances.[1–3] Cyclopropanecarboxylic acid derivatives are successfully used in medicine and agriculture. Naturally occurring and synthetic pyrethroids have found wide application as insecticides.[1,4]

Due to extensive research into electrochemistry of organic compounds conducted over the past three decades, electrosynthesis has become a competitive method of modern organic chemistry.[5] Electrochemical synthesis is assuming increasing importance because of its great and, in some cases, unique possibilities for performing various transformations of organic compounds.[6]

The use of mediators and mediator systems for electroreduction and electrooxidation of organic compounds was an important stage in the development of electrosynthesis. Among numerous mediators, a halide anion—halogen system is one of the most promising mediator systems for application in organic synthesis.[7]

The present study continues investigations on electrochemical transformations of CH-acids, such as malononitrile, cyanoacetic ester, and malonic ester, into functionalized cyclopropanes in the presence of mediators, viz., alkali metal halides. In our earlier studies of electrocatalytic oxidation of organic compounds in the presence of mediators, we have performed electrochemical cyclotrimerization of malonic[8] and cyanoacetic esters,[9] transformations of aldehydes and cyanoacetic ester[10] into functionalized cyclopropanes, and ketones and malononitrile into 3,3-disubstituted tetracyanocyclopropanes.[11]

The latter process is an electrochemical variant of the Wideqvist reaction, i.e., the reaction of bromomalononitrile with ketones in the presence of stoichiometric amounts of sodium iodide.[12]

The electrochemical modification of this reaction is performed with the use of malononitrile instead of bromomalononitrile and catalytic amounts of sodium bromide, which is completely regenerated during the reaction.[13]

Several years ago, we developed a new procedure for the synthesis of functionalized cyclopropanes based on simultaneous electrolysis of CH-acids and activated olefins[14,15] (Scheme 1).

Recently, we have performed the 'one-pot' electrocatalytic transformation of malonic ester and alkylidenemalononitriles into 3-substituted 2,2-dicyanocyclopropane-1,1-

Keywords: Electrolysis; Stereoselectivity; Electrocatalytic transformation; Mediators; Malonate; Alkylidenecyanoacetates; Substituted cyclopropanes.
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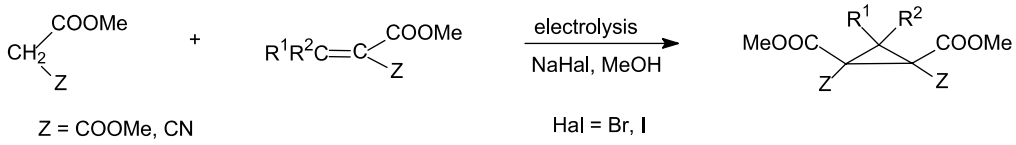
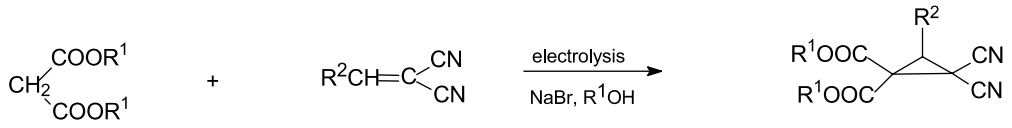
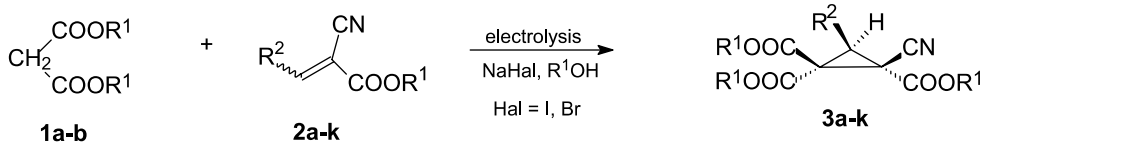
0040–4020/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tet.2006.02.027



Scheme 1.



Scheme 2.



Scheme 3.

dicarboxylic acid esters. This process was carried out in alcohols in an undivided cell with the use of NaBr as mediator (Scheme 2).[16]

In the present paper, we describe our results on investigation of the stereoselective 'one-pot' electrocatalytic transformation of malonic ester and alkylidenecyanoacetic esters into (*E*) isomers of trialkyl esters 3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylic acids (**3a**–**k**). This reaction was carried out in alcohols (methanol or ethanol) in an undivided cell with the use of NaBr or NaI as a mediator (Scheme 3, Table 1); for a preliminary communication, see Ref. 17.

2. Results and discussion

Electrolysis of methyl malonate **1a** or ethyl malonate **1b** in the presence of alkylidenecyanoacetic esters **2a**–**k** in methanol or ethanol, respectively, was carried out under constant current mode in an undivided cell equipped with a graphite anode and an iron cathode until complete conversion of malonic and alkylidenecyanoacetic esters was achieved.

The optimum temperature for simultaneous electrolysis of malonic ester and alkylidenecyanoacetic esters, as in

Table 1. Electrocatalytic transformation of malonic esters **1a**,**b** and alkylidenecyanoacetic esters **2a**–**k** into cyclopropanes **3a**–**k**[a]

Malonic ester	R^1	Alkylidenecyanoacetic ester	R^2	Temperature (°C)	Mediator	Cyclopropane	Yield (%)[b]
1a	Me	**2a**	Ph	20	NaBr	**3a**	(35)[c]
1a	Me	**2a**	Ph	10	NaBr	**3a**	(61)[c]
1a	Me	**2a**	Ph	0	NaBr	**3a**	81 (92)[c]
1b	Et	**2b**	Ph	0	NaBr	**3b**	82
1a	Me	**2a**	Ph	0	NaI	**3a**	67
1a	Me	**2c**	4-MeC_6H_4	0	NaBr	**3c**	83
1a	Me	**2d**	4-$MeOC_6H_4$	0	NaBr	**3d**	87
1a	Me	**2e**	2-ClC_6H_4	0	NaBr	**3e**	81
1a	Me	**2f**	4-ClC_6H_4	0	NaBr	**3f**	87
1b	Et	**2g**	4-ClC_6H_4	0	NaBr	**3g**	83
1a	Me	**2h**	3-BrC_6H_4	0	NaBr	**3h**	93
1a	Me	**2i**	Me	0	NaBr	**3i**	88
1a	Me	**2i**	Me	0	NaI	**3i**	71
1a	Me	**2j**	Et	0	NaBr	**3j**	79
1a	Me	**2k**	*n*-Pr	0	NaBr	**3k**	75

[a] Malonic ester (10 mmol), alkylidenecyanoacetic ester (10 mmol), mediator (5 mmol), alcohol (20 ml), Fe cathode, C anode, current density 100 mA/cm^2, 3.0 F/mol of electricity was passed.
[b] Based on the isolated cyclopropane.
[c] The yields given in parentheses were determined from ^{1}H NMR spectroscopic and GLC data.

the case of co-electrolysis of malonic ester and alkylidenemalononitrile, is 0 °C. An increase in the temperature up to +10 or +20 °C (at +20 °C, electrolysis of malonic ester in the presence of alkylidenemalonates was performed)[14] leads to a substantial decrease in the yield of cyclopropanes **3a–k**, and the reaction gives a considerable amount of oligomeric compounds, which hinders isolation of cyclopropanes **3a–k**.

As in the analogous reactions of malonic ester with alkylidenemalonates[14] or alkylidenemalononitriles,[16] reactions of cyanoacetic ester with alkylidenecyanoacetic esters,[15] and reactions of malononitrile with alkylidenemalononitriles,[18] sodium bromide is a more efficient as mediator than NaI for the electrocatalytic process studied. Thus, with the use of NaBr as a mediator the cyclopropanes **3a–k** were obtained in higher yields.

In co-electrolysis of ester **1a** and benzylidenecyanoacetic ester **2a** when a quantity of electricity was less than the optimum value of 3 F/mol (0.5 and 1.0 F/mol), trimethyl 3-cyanopropane-2-phenyl-1,1,3-tricarboxylate (**4**) (57 and 36% yields, respectively) was detected by ^{1}H NMR spectroscopy along with cyclopropane **3a** (16 and 37% yields, respectively).

The formation of only one of two possible isomers of cyclopropanes **3a–k** was established by the ^{1}H and ^{13}C NMR spectroscopic data. The structures of **3a** and **3i** were established by X-ray diffraction.[17] Taking into account the factor of the minimum steric hindrance in the cyclopropane ring formation, all cyclopropanes **3** should have a structure containing the cyano group and R^2-substituent in cis arrangement (Fig. 1).

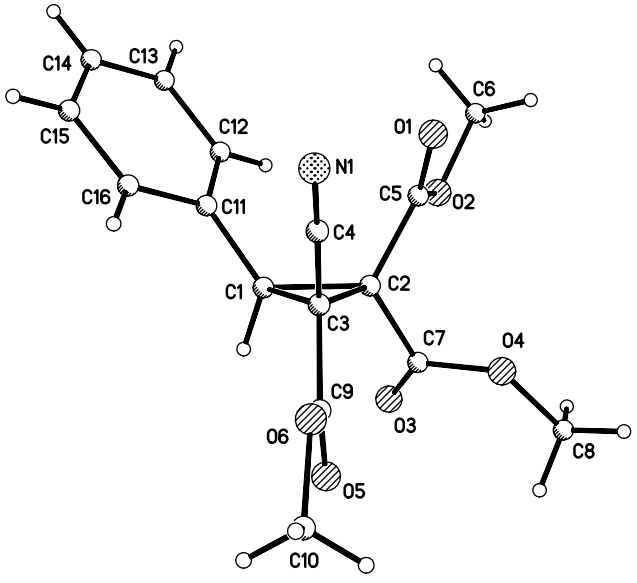
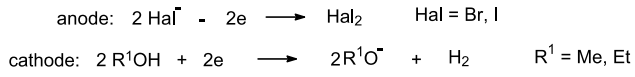


Figure 1. Molecule structure of **3a**.

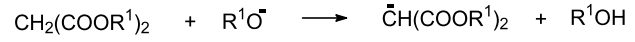
Based on our results and the data on the electrochemical transformation of malonic ester and alkylidenemalonic esters[14] or alkylidenemalononitriles[16] into functionalized cyclopropanes, we suggest the following mechanism for the stereoselective electrocatalytic transformation of malonic ester and alkylidenecyanoacetic esters into (*E*)-3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylic acid esters.

Reactions at electrodes are usual for the mediator system consisting of the halide anion and molecular halogen in alcohols. These reactions involve the formation of halogen at the anode and liberation of hydrogen at the cathode resulting in the generation of alkoxide ions (Scheme 4):



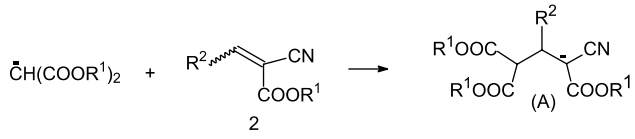
Scheme 4.

Then malonate anions appear in solution as a result of the reaction of the electrogenerated alkoxide ions with malonic ester (Scheme 5):



Scheme 5.

The reaction of the malonate anion with activated olefin **2** yields the anion (**A**) (Scheme 6):



Scheme 6.

Subsequent halogenation of the anion **A** and cyclization under the action of alkoxide ions could afford functionalized cyclopropane **3** (Scheme 7).

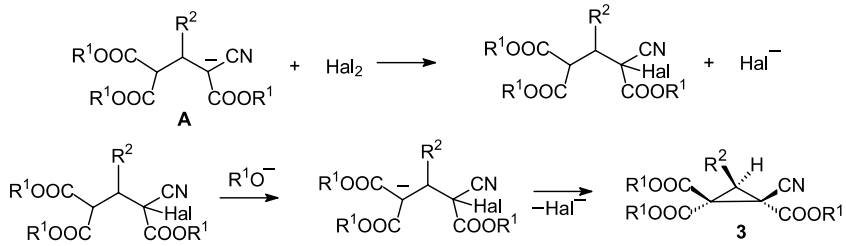
However, this mechanism could provide the observed stereoselectivity of the cyclopropane **3** formation only if halogenation of the anion **A** occurred stereoselectively.

The more probable is the existence of another process involving the initial halogen transfer by the Hal_T^+ transfer mechanism[19] giving rise to an anion (**B**) followed by thermodynamically controlled cyclization (Scheme 8).

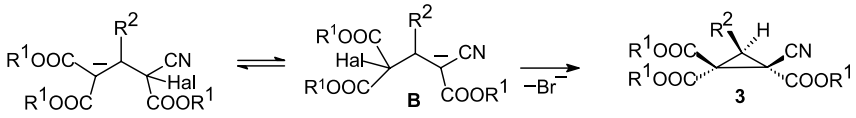
Stereoselective thermodynamically controlled cyclization was also observed in electrocatalytic cyclotrimerization of cyanoacetic ester into *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylic acid ester.[9]

Earlier, NaI was shown to be a more efficient mediator for electrocatalytic cyclization of 2-substituted propane-1,1,3,3-tetracarboxylic acid esters than NaBr.[20] This fact is associated with the higher selectivity of iodine as an oxidant of the 2-substituted propane-1,1,3,3-tetracarboxylic acid esters anion in the presence of alkoxide ions compared to bromine.

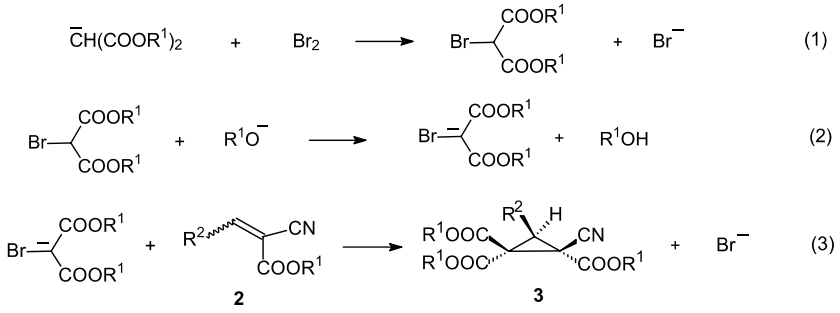
In the electrocatalytic process under consideration, NaBr is a more efficient mediator for the stereoselective transformation of malonic ester and alkylidenecyanoacetic esters into (*E*)-3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylic acid esters **3a–k** compared to NaI.



Scheme 7.



Scheme 8.



Scheme 9.

Most likely, this result is attributed to the presence of another way of the electrocatalytic process (Scheme 9).

The fact that electrolysis of malonic ester in alcohols in the presence of NaBr in an undivided cell produces the bromomalonate anion has been established previously.[21]

The high efficiency of NaBr as a mediator for the reaction pathway shown in Scheme 9 is associated with the fact that bromomalonic ester is a stronger CH-acid compared to iodomalonic ester due to which the step (2) involving the proton abstraction by the alkoxide ion occurs more rapidly in bromomalonic ester than in iodomalonic ester. Besides, it is also probable that the addition of the bromomalonate anion to activated olefin **2** occurs more rapidly in the step (3).

The formation of 3-substituted-2-cyanocyclopropane-1,1,2-tricarboxylic acid esters **3a**,**j** was also investigated by performing the alternative electrolysis of cyanoacetic ester and alkylidenemalonic esters **5** (Table 2, Scheme 10).

However, as it follows from the data of Table 2, in this case the synthesis of cyclopropanes **3** requires that the electrolysis was performed at lower temperature (at −20 °C rather than at 0 °C, see Tables 1 and 2).

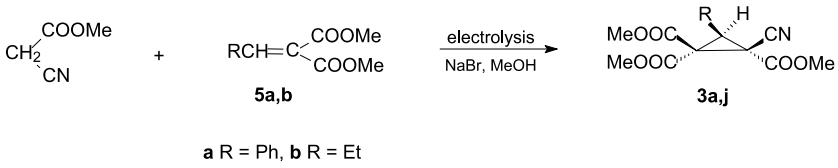
It should also be noted that the reaction performed according to Scheme 10, even at −20 °C, produces cyclic esters **3a**,**j** (Table 2) in 30–50% lower yields than those obtained as described above (Table 1) by simultaneous electrolysis of malonic ester and alkylidenecyanoacetic esters at 0 °C.

Table 2. Stereoselective electrocatalytic transformation of methyl cyanoacete and alkylidenemalonic esters **5a**,**b** into cyclopropanes **3a**,**j**[a]

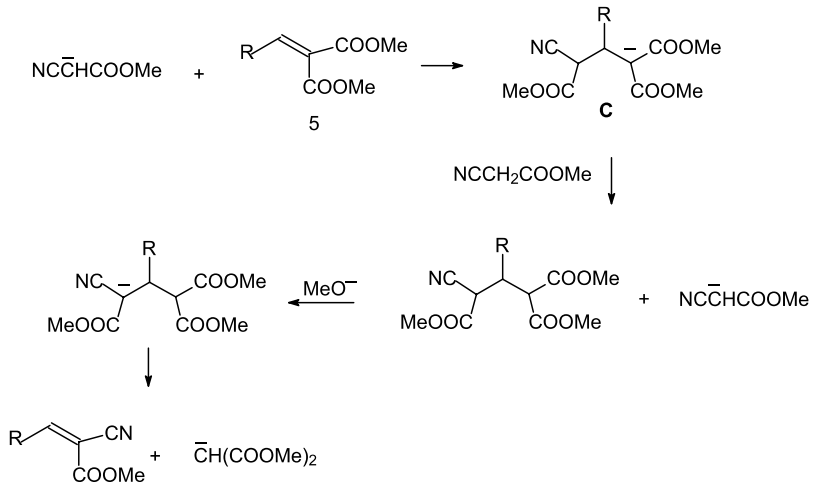
Alkylide-nemalonic ester	R	Temperature (°C)	Mediator	Cyclopropane	Yield (%)[b]
5a	Ph	0	NaBr	**3a**	26
5a	Ph	−10	NaBr	**3a**	35
5a	Ph	−20	NaBr	**3a**	43
5a	Ph	−20	NaI	**3a**	34
5b	Et	0	NaBr	**3j**	33
5b	Et	−10	NaBr	**3j**	45
5b	Et	−20	NaBr	**3j**	51
5b	Et	−20	NaI	**3j**	43

[a] Methyl cyanoacete (10 mmol), **5a** or **5b** (10 mmol), a mediator (5 mmol), MeOH (20 ml), Fe cathode, C anode, the current density 100 mA/cm^2, 3.0 F/mol of electricity was passed.
[b] The ^{1}H NMR spectroscopic and GLC data.

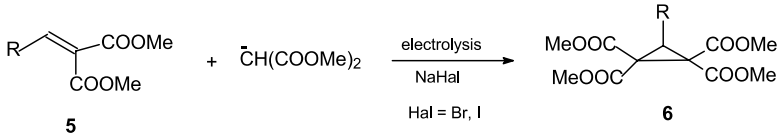
The lower yields of cyclopropanes **3** prepared according to the second approach (Table 2) are, apparently, attributable to the following facts: (1) alkylidenemalonic esters are more prone to reductive dimerization[22] compared to the competitive addition of cyanoacetate or halocyanoacetate anions; (2) the oligomerization of cyanoacetic ester in the presence of bases,[9,23] unlike malonic ester, which is stable under these conditions; (3) the reaction proceeds through the intermediate formation of the anion (**C**), which can undergo the transformation and decomposition giving rise to the malonate anion according to the Scheme 11.



Scheme 10.



Scheme 11.



Scheme 12.

Transformations analogous to those presented in Scheme 11 have been described earlier for the reactions of substituted benzylidenemalononitriles with the cyanoacetate anion.[24]

Electrolysis of malonate anions thus generated and alkylidenemalonic ester produces cyclic ester **6** (Scheme 12).

Electrolysis of methyl cyanoacetate and benzylidenemalonic ester **5a** at 0, −10, and −20 °C afforded a mixture, in which cyclic ester **3a** (26, 35, and 43% yields, respectively), ester **6** (R=Ph) (23, 17, and 7%, respectively), and tetramethyl 2,3-diphenylbutane-1,1,4,4-tetracarboxylate (**7**) (18, 13, and 6%, respectively) were detected by ^{1}H NMR spectroscopy and GLC analysis.

3. Conclusion

To summarize, we have performed simultaneous electrolysis of malonic ester and alkylidenecyanoacetic esters in an undivided cell in the presence of a sodium halide as mediator. With this method was realized the 'one-pot' stereoselective synthesis of (*E*)-3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylic acid esters in 75–90% yields. These compounds can be synthesized according to conventional methods of organic chemistry in two steps: (1) halogenation of malonic ester and (2) the addition of halomalonic ester to the double bond of alkylidenecyanoacetic ester followed by cyclization.[25]

Thus, we developed a convenient and simple electrocatalytic procedure for the stereoselective transformation of malonic ester and alkylidenecyanoacetic esters into (*E*)-3-substituted 2-cyanocyclopropane-1,1,2-tricarboxylic acid esters. This method requires the use of standard and commercially available reagents, inexpensive apparatus, and an undivided cell. The techniques for electrolysis and isolation of the reaction products are simple and convenient to use both under laboratory conditions and in large-scale apparatus.

4. Experimental

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. GLC analyses were carried out on a LKhM-80 chromatograph with a flame-ionisation detector, 3 m×3 mm glass columns packed with 5% OV-17 on Inerton (0.16–0.20 mm) or 10% FFAP on Chromaton N-Super (0.13–0.16 mm), respectively. ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250, Bruker AM-300 and Varian Unity 500-PLUS spectrometer instruments operating at 250, 300 and 500 MHz, respectively. The chemical shifts were measured on the δ scale

relative to Me_4Si. Mass-spectra (70 eV) were determined directly using Finningan MAT INCOS 50 spectrometer.

X-ray diffraction experiments were carried out on CAD4 Siemens P3/PC (**3a**) and Enraf-Nonius (**3i**) difractometers (T 293 K, graphite monochromated Mo K_α radiation, $\theta_{max}=25°$) The structures **3a** and **3i** were solved by direct methods and refined by the full-matrix least-squares technique on F^2_{hkl} in the anisotropic approximation. H atoms were located from the difference Fourier synthesis and then refined isotropically. The final values of R factors were as follows: $R_1=0.039$ (912 observed reflections), $wR_2=0.2348$ (for all 1547 reflections) for **3a**, and $R_1=0.0580$ (1704 observed reflections), $wR_2=0.1278$ (for all 2226 reflections used in refinement) for **3i**. All calculations were carried out with the complex of programs SHELXTL.

PLUS 5 [Sheldrick, G. M. *SHELXTL Software Reference Manual*, Version 5, Siemens Industrial Automation, Inc.: Madison, 1994].

Crystallographic data for **3a** and **3i** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 284947 and CCDC 284948. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Malonic and cyanoacetic esters were purchased from Aldrich. Alkylidenecyanoacetic esters **2a**–**k** and benzylidene- and propylidenemalonic esters **5a**,**b** were prepared by Knoevenagel condensation[26] of the corresponding aldehydes and cyanoacetic or malonic esters (Merck and Aldrich).

4.1. General procedure for simultaneous electrolysis of malonic ester and alkylidenecyanoacetic esters

A solution of malonic ester **1a**,**b** (10 mmol), alkylidenecyanoacetic ester **2a**–**k** (10 mmol), and a mediator (5 mmol) in MeOH or EtOH (20 ml) was electrolyzed in an undivided cell equipped with C-anode and Fe-cathode (the electrode surface area was 5 cm^2) thermometer, external cooling and magnetic stirring at a constant current density of 100 mA/cm^2 by passing 3.0 F/mol of electricity. At the end of electrolysis, the solution was additionally cooled to −10 °C. The precipitate of cyclopropane **3** that formed was filtered off and washed with cooled to 5 °C alcohol. An additional amount of cyclopropane **3** was isolated as follows. The reaction mixture was concentrated, extracted with chloroform, washed with water, and dried over Na_2SO_4. The chloroform was distilled off. The residue was crystallised from an acetone–hexane or diethyl ether–hexane mixture, and cyclopropane **3** was isolated. After evaporation of the reaction mixture, cyclopropanes **3b**,**c**,**g** were isolated by flash chromatography (eluent chloroform/hexane 1:1) and cyclopropanes **3j**,**k** were isolated by vacuum distillation.

4.1.1. (*E*)-Trimethyl 2-cyanocyclopropane-3-phenyl-1,1,2-tricarboxylate (3a). Yield 2.57 g (81%), white solid, mp 140–142 °C. ^{1}H NMR (CD_3CN), δ: 3.70 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 3.96 (s, 1H, CH), 7.38 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 30.6 (C), 39.6 (CH), 47.7 (C), 53.5 (CH_3O), 53.7 (CH_3O), 54.5 (CH_3O), 112.4 (CN), 128.5, 128.7, 128.8, 129.3 (Ph), 162.7 (OC=O), 164.27 (OC=O), 164.8 (OC=O). MS (70 eV): m/z (relative intensity %): 317 (M^+, 8), 286 (9), 258 (100), 198 (71), 121 (52), 59 (72). IR (KBr): ν_{max} 2252, 1772, 1756, 1436, 1232. Anal. Calcd for $C_{16}H_{15}NO_6$: C, 60.57; H, 4.76; N, 4.41. Found: C, 60.39; H, 4.61; N, 4.25.

Crystal data for **3a**: $C_{16}H_{15}NO_6$, $M=317.29$, rhombic, space group $P2_12_12_1$, $a=9.715(5)$ Å, $b=10.693(5)$ Å, $c=15.013(8)$ Å, $V=1559.9(14)$ Å^3, $Z=4$, $D_c=1.351$ g cm^{-3}.

4.1.2. (*E*)-Triethyl 2-cyanocyclopropane-3-phenyl-1,1,2-tricarboxylate (3b). Yield 3.05 g (85%), colourless oil. ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, CH_3, $J=7.1$ Hz), 1.29 (t, CH_3, $J=7.1$ Hz), 1.38 (t, CH_3, $J=7.1$ Hz), 3.93 (s, 1H, CH), 4.12 (q, 2H, CH_2O, $J=7.1$ Hz), 4.20–4.45 (m, 4H, CH_2O), 7.25–7.51 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 13.4 (CH_3), 13.6 (CH_3), 13.8 (CH_3), 30.6 (C), 39.0 (CH), 47.7 (C), 62.7 (CH_2O), 62.8 (CH_2O), 64.0 (CH_2O), 112.5 (CN), 128.5, 128.6, 128.9, 129.6 (Ph), 162.3 (OC=O), 163.7 (OC=O), 164.2 (OC=O). MS (70 eV): m/z (relative intensity %): 359 (M^+, 3), 314 (5), 286 (100), 258 (32), 212 (23), 140 (32), 105 (17). IR (KBr): ν_{max} 2256, 1752, 1448, 1264, 1232. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.32; H, 5.93; N, 3.81.

4.1.3. (*E*)-Trimethyl 2-cyanocyclopropane-3-(4-methylphenyl)-1,1,2-tricarboxylate (3c). Yield 2.75 g (83%), white solid, mp 72–74 °C. ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3H, CH_3), 3.72 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.89 (s, 1H, CH), 3.91 (s, 3H, OCH_3), 7.18 (d, 2H, $J=8.3$ Hz), 7.25 (d, 2H, $J=8.3$ Hz). ^{13}C NMR ($CDCl_3$), δ: 21.0 (CH_3), 30.5 (C), 39.4 (CH), 47.6 (C), 53.4 (CH_3O), 53.6 (CH_3O), 54.4 (CH_3O), 112.4 (CN), 127.0, 128.2, 129.4, 138.5 (Ar), 162.6 (OC=O), 164.2 (OC=O), 164.8 (OC=O). MS (70 eV): m/z (relative intensity %): 331 (M^+, 13), 300 (7), 272 (68), 212 (100), 135 (52), 59 (76). IR (KBr): ν_{max} 2252, 1756, 1748, 1436, 1232. Anal. Calcd for $C_{17}H_{17}NO_6$: C, 61.63; H, 5.17; N, 4.23. Found: C, 61.44; H, 4.98; N, 4.14.

4.1.4. (*E*)-Trimethyl 2-cyanocyclopropane-3-(4-methoxyphenyl)-1,1,2-tricarboxylate (3d). Yield 3.01 g (87%), white solid, mp 110–112 °C. ^{1}H NMR ($CDCl_3$), δ: 3.72 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 3.87 (s, 1H, CH), 3.91 (s, 3H, CH_3O), 6.88 (d, 2H, Ar, $J=8.2$ Hz), 7.29 (d, 2H, Ar, $J=8.2$ Hz). ^{13}C NMR ($CDCl_3$), δ: 30.7 (C), 39.3 (CH), 47.8 (C), 53.5 (CH_3O), 53.7 (CH_3O), 54.5 (CH_3O), 55.2 (CH_3O), 112.5 (CN), 114.2, 124.2, 129.7, 159.7 (Ar), 162.7 (OC=O), 164.3 (OC=O), 164.8 (OC=O). MS (70 eV): m/z (relative intensity %): 347 (M^+, 57), 316 (3), 288 (13), 228 (100), 170 (39), 151 (38), 59 (82). IR (KBr): ν_{max} 2252, 1756, 1752, 1440, 1240. Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.61; H, 4.84; N, 3.92.

4.1.5. (*E*)-Trimethyl 3-(2-chlorophenyl)-2-cyanocyclopropane-1,1,2-tricarboxylate (3e). Yield 2.85 g (81%), white solid, mp 97–99 °C. ^{1}H NMR ($CDCl_3$), δ: 3.78 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 3.88 (s, 1H, CH), 3.94 (s, 3H, CH_3O), 7.25–7.48 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$), δ: 31.4

(C), 38.6 (CH), 47.4 (C), 53.6 (CH_3O), 53.7 (CH_3O), 54.7 (CH_3O), 112.2 (CN), 127.1, 127.5, 129.9, 130.1, 134.9 (Ar), 162.9 (OC=O), 164.2 (OC=O), 164.8 (OC=O). MS (70 eV): *m/z* (relative intensity %): 351 (M^+, 8), 320 (7), 292 (100), 232 (36), 155 (33), 59 (89). IR (KBr): ν_{max} 2256, 1760, 1748, 1440, 1236. Anal. Calcd for $C_{16}H_{14}ClNO_6$: C, 54.64; H, 4.01; Cl, 10.08; N, 3.98. Found: C, 54.43; H, 3.95; Cl, 9.87; N, 3.84.

4.1.6. (*E*)-Trimethyl 3-(4-chlorophenyl)-2-cyanocyclopropane-1,1,2-tricarboxylate (3f). Yield 3.06 g (87%), white solid, mp 73–75 °C. ^{1}H NMR ($CDCl_3$), δ: 3.76 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 3.87 (s, 1H, CH), 3.93 (s, 3H, CH_3O), 7.23–7.45 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$), δ: 30.5 (C), 38.6 (CH), 47.5 (C), 53.5 (CH_3O), 53.6 (CH_3O), 54.6 (CH_3O), 112.1 (CN), 127.7, 129.0, 129.8, 134.8 (Ar), 162.4 (OC=O), 164.0 (OC=O), 164.5 (OC=O). MS (70 eV): *m/z* (relative intensity %): 351 (M^+, 8), 320 (6), 292 (72), 232 (51), 174 (21), 155 (36), 59 (100). IR (KBr): ν_{max} 2256, 1756, 1744, 1440, 1232. Anal. Calcd for $C_{16}H_{14}ClNO_6$: C, 54.64; H, 4.01; Cl, 10.08; N, 3.98. Found: C, 54.71; H, 4.09; Cl, 10.15; N, 3.75.

4.1.7. (*E*)-Triethyl 3-(4-chlorophenyl)-2-cyanocyclopropane-1,1,2-tricarboxylate (3g). Yield 3.27 g (83%), colourless oil. ^{1}H NMR ($CDCl_3$), δ: 1.08 (t, CH_3, J=7.1 Hz), 1.24 (t, CH_3, J=7.1 Hz), 1.35 (t, CH_3, J=7.1 Hz), 3.91 (s, 1H, CH), 4.15–4.45 (m, 6H, CH_2O), 7.20–7.45 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$), δ: 13.47 (CH_3), 13.53 (CH_3), 13.8 (CH_3), 33.1 (C), 38.2 (CH), 46.7 (C), 62.8 (CH_2O), 62.9 (CH_2O), 64.1 (CH_2O), 112.4 (CN), 128.9, 129.4, 129.9, 133.8 (Ar), 163.4 (OC=O), 166.1 (OC=O), 167.5 (OC=O). MS (70 eV): *m/z* (relative intensity %): 393 (M^+, 6), 348 (7), 320 (100), 246 (98), 202 (91), 174 (78), 169 (78). IR (KBr): ν_{max} 2252, 1752, 1736, 1440, 1260. Anal. Calcd for $C_{19}H_{20}ClNO_6$: (%): C, 57.95; H, 5.12; Cl, 9.00; N, 3.56. Found: C, 57.74; H, 5.15; Cl, 8.91; N, 3.43.

4.1.8. (*E*)-Trimethyl 3-(3-bromophenyl)-2-cyanocyclopropane-1,1,2-tricarboxylate (3h). Yield 3.88 g (98%), yellow solid, mp 89–91 °C. ^{1}H NMR ($CDCl_3$), δ: 3.73 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.87 (s, 1H, CH), 3.89 (s, 3H, CH_3O), 7.20–7.33 (m, 2H, Ar), 7.40–7.50 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$), δ: 30.4 (C), 38.4 (CH), 47.3 (C), 53.6 (CH_3O), 53.7 (CH_3O), 54.6 (CH_3O), 111.9 (CN), 122.4, 128.1, 130.3, 131.46, 131.53, 131.7 (Ar), 162.4 (OC=O), 163.8 (OC=O), 164.4 (OC=O). MS (70 eV): *m/z* (relative intensity %): 397 (M^+, 15), 395 (M^+, 14), 364 (3), 366 (2), 338 (61), 336 (78), 278 (28), 276 (34), 201 (25), 199 (27), 59 (100). IR (KBr): ν_{max} 2268, 1756, 1746, 1440, 1232. Anal. Calcd for $C_{16}H_{14}BrNO_6$: C, 48.51; H, 3.56; Br, 20.17; N, 3.54. Found: C, 48.35; H, 3.47, Br, 19.93; N, 3.29.

4.1.9. (*E*)-Trimethyl 2-cyanocyclopropane-3-methyl-1,1,2-tricarboxylate (3i). Yield 2.24 g (88%), white solid, mp 87–89 °C. ^{1}H NMR ($CDCl_3$), δ: 1.45 (d, 3H, CH_3, J=6.7 Hz), 2.67 (q, 1H, CH, J=6.7 Hz), 3.70 (s, 3H, CH_3O), 3.79 (s, 6H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 9.6 (CH_3), 31.0 (C), 31.8 (CH), 47.0 (C), 53.61 (CH_3O), 53.8 (CH_3O), 54.4 (CH_3O), 112.6 (CN), 163.2 (OC=O), 164.4 (OC=O), 164.9 (OC=O). MS (70 eV): *m/z* (relative intensity %): 255 (M^+, 2), 224 (8), 196 (51), 164 (32), 137 (7), 92 (11), 59 (100). IR (KBr): ν_{max} 2256, 1756, 1744, 1444, 1240. Anal. Calcd for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.55; H, 4.98; N, 5.38.

Crystal data for **3i**: $C_1H_{13}NO_6$, M=255.22, monoclinic, space group $P2_1/n$, a=8.972(3) Å, b=15.159(7) Å, c=9.732(4) Å, β=106.89(3)°, V=1266.5(9) Å^3, Z=4, D_c=1.339 g cm^{-3}.

4.1.10. (*E*)-Trimethyl 2-cyano-3-ethylcyclopropane-1,1,2-tricarboxylate (3j). Yield 2.13 g (79%), colourless oil, bp 131–143 °C (0.10 Torr). ^{1}H NMR ($CDCl_3$), δ: 1.03 (t, 3H, CH_3, J=7.3 Hz), 1.68–1.84 (m, 2H, CH_2), 2.61 (t, 1H, CH, J=7.3 Hz), 3.72 (s, 3H, CH_3O), 3.81 (s, 6H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 12.2 (CH_3), 18.0 (CH_2), 30.4 (C), 38.2 (CH), 46.8 (C), 53.5 (CH_3O), 53.7 (CH_3O), 54.3 (CH_3O), 112.5 (CN), 163.25 (OC=O), 164.4 (OC=O), 164.8 (OC=O). MS (70 eV): *m/z* (relative intensity %): 269 (M^+, 5), 238 (12), 210 (63), 178 (57), 146 (29), 133 (37), 59 (100). IR (KBr): ν_{max} 2252, 1755, 1748, 1436, 1238. Anal. Calcd for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.62; N, 5.20. Found: C, 53.35; H, 5.48; N, 5.31.

4.1.11. (*E*)-Trimethyl 2-cyanocyclopropane-3-propyl-1,1,2-tricarboxylate (3k). Yield 2.18 g (77%), colourless oil, bp 140–142 °C (0.08 Torr). ^{1}H NMR ($CDCl_3$), δ: 0.98 (t, 3H, CH_3, J=7.3 Hz), 1.46–1.58 (m, 2H, CH_2), 1.73–1.83 (m, 2H, CH_2), 2.62 (t, 1H, CH, J=7.3 Hz), 3.73 (s, 3H, CH_3O), 3.82 (s, 6H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 13.3 (CH_3), 21.2 (CH_2), 26.2 (CH_2), 30.4 (C), 36.7 (CH), 46.6 (C), 53.4 (CH_3O), 53.5 (CH_3O), 54.2 (CH_3O), 112.6 (CN), 163.3 (OC=O), 164.4 (OC=O), 164.9 (OC=O). MS (70 eV): *m/z* (relative intensity %): 283 (M^+, 2), 252 (17), 224 (71), 192 (65), 160 (28), 132 (88), 59 (100). IR (KBr): ν_{max} 2252, 1748, 1742, 1436, 1236. Anal. Calcd for $C_{13}H_{17}NO_6$: (%): C, 55.12; H, 6.05; N, 4.94. Found: C, 54.93; H, 6.11; N, 4.71.

4.1.12. Trimethyl 2-phenyl-3-cyanopropane-1,1,3-tricarboxylate (4). The solution of Na (1 mmol) in 5 ml of methanol was added to solution of dimethyl malonate (10 mmol) and methyl benzylidenecyanoacetate (10 mmol) at room temperature. After 30 min the resulting solid was filtered off. The solvent was evaporated, the residue was extracted with 30 ml of chloroform, washed with water and dried over Na_2SO_4. Chloroform was removed under reduced pressure and the residue together with the first solid part were crystallised from methanol. After crystallization **4** was obtained as a mixture of two diastereomers (ratio 10:1), 2.55 g, 85% yield, white solid, mp 87–89 °C. Main diastereomer ^{1}H NMR ($CDCl_3$), δ: 3.52 (s, 3H, OCH_3), 3.77 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 4.16 (dd, 1H, CH, J_1=5 Hz, J_2=11 Hz), 4.25 (d, 1H, CH, J=5 Hz), 4.38 (d, 1H, CH, J=11 Hz), 7.30–7.40 (m, 5H, Ph). Minor diastereomer ^{1}H NMR ($CDCl_3$), δ: 3.47 (s, 3H, OCH_3), 3.63 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 4.14 (dd, 1H, CH, J_1=5 Hz, J_2=11 Hz), 4.18 (d, 1H, CH, J=11 Hz), 4.54 (d, 1H, CH, J=5 Hz), 7.30–7.40 (m, 5H, Ph). Main diastereomer ^{13}C NMR ($CDCl_3$), δ: 41.86 (CH), 44.81 (CH), 52.68, 53.10, 53.49, 54.17 (3OCH_3 and CH), 115.07 (CN), 128.02, 128.75, 128.93, 136.20 (Ph), 165.20 (OC=O), 167.12 (OC=O), 168.00 (OC=O). Minor diastereomer ^{13}C NMR ($CDCl_3$), δ: 41.89 (CH), 43.97 (CH), 53.08, 53.25, 53.33, 53.75 (3OCH_3 and CH), 114.85 (CN), 128.48,

128.66, 128.71, 134.68 (Ph), 164.86 (OC═O), 166.85 (OC═O), 167.97 (OC═O). IR (KBr): ν_{max} 2260, 1732, 1456, 1252, 1228. Anal. Calcd for $C_{16}H_{17}NO_6$: (%): C, 60.18; H, 5.37; N, 4.39. Found: C, 60.25; H, 5.26; N, 4.28.

4.1.13. Tetramethyl 3-phenylcyclopropane-1,1,2,2-tetracarboxylate (6). The title compound was prepared according to a known procedure,[14] mp 85–86 °C (cf. lit. data:[27] mp 87 °C). ^{1}H NMR ($CDCl_3$), δ: 3.66 (s, 6H, CH_3O), 3.78 (s, 1H, CH), 7.20–7.35 (m, 5H, Ph).

4.1.14. Tetramethyl 2,3-diphenylbutane-1,1,4,4-tetracarboxylate (7). The title compound was prepared according to a known procedure[22] in 58% yield as a mixture of *meso* and D,L isomers in a ratio of 2:1. The *meso* form was isolated by crystallization from methanol. The D,L form was isolated by column chromatography of the residue obtained after crystallization; a 2:1 diethyl ether/hexane mixture was used as the eluent. The *meso* form **7** was also isolated by crystallization from the reaction mixture, which was obtained by simultaneous electrolysis of methyl cyanoacetate and benzylidenemalonic ester **5a** at 0 °C (Table 2), in 9% yield. The physicochemical and spectroscopic characteristics of the *meso*- and D,L-**7** forms were analogous to those described earlier.[22]

Acknowledgements

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32068) and the Program for Support of Leading Scientific Schools (Grant No. 2121.2003.3).

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