Electrocatalytic transformation of dialkyl malonates and arylidene- or alkylidenemalononitriles into dialkyl esters of 3-substituted 2,2-dicyanocyclopropane-1,1-dicarboxylic acids

M. N. Elinson,[a] S. K. Feducovich,[a] T. A. Zaimovskaya,[b] A. N. Vereshchagin,[a] S. V. Gorbunov,[a] and G. I. Nikishin[a]*

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: elinson@ioc.ac.ru*
[b]*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 230 2224. E-mail: zatan@ips.ac.ru*

Electrolysis of alcoholic solutions of dialkyl malonates and arylidene- or alkylidenemalononitriles in the presence of NaBr in an undivided cell gave dialkyl esters of 3-substituted 2,2-dicyanocyclopropane-1,1-dicarboxylic acids in 60—90% yields.

Key words: electrolysis, electrocatalytic transformation, dialkyl malonates, arylidenemalononitriles, alkylidenemalononitriles, mediators, substituted cyclopropanes.

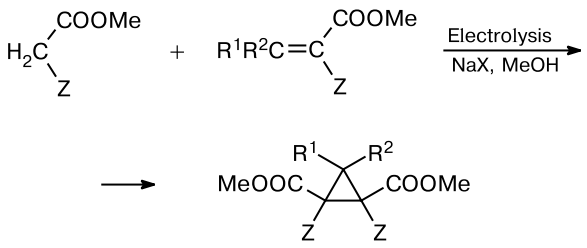
Functionally substituted cyclopropanes are physiologically active in a wide range.[1—4] Therefore, the development of simple and efficient methods for syntheses of functionally substituted cyclopropanes remains important.

Electrosynthesis is a competitive method of the modern organic chemistry due to many studies on the electrochemistry of organic compounds appeared during the last three decades.[5,6] The use of mediators and mediator systems for electroreduction and electrooxidation of organic compounds allowed the electrolysis efficiency to increase. Among numerous mediators, the redox system halide anion—halogen seems to be one of the most promising for use in organic synthesis.[7]

In this work, we continue the series of studies on electrochemical transformations of CH-acids, such as malononitrile, and esters of cyanoacetic and malonic acids, into functionally substituted cyclopropanes using mediators, *viz.*, alkaline metal halides. In our previous studies on electrocatalytic oxidation of organic compounds in the presence of mediators, we carried out the electrochemical cyclotrimerization of esters of malonic[8] and cyanoacetic acids[9] and transformation of aldehydes and ethyl cyanoacetate into functionally substituted cyclopropanes,[10] while ketones and malononitrile were converted into 3,3-disubstituted tetracyanocyclopropanes.[11] The latter is an electrochemical analog of the Wideqvist reaction, *i.e.*, interaction of bromomalononitrile with ketones in the presence of stoichiometric amounts of sodium iodide.[12] In the electrochemical version, malononitrile is used instead of bromomalononitrile, and catalytic amounts of sodium bromide are completely regenerated during the process.[13]

We have recently proposed a new approach to the synthesis of functionally substituted cyclopropanes: combined electrolysis of CH-acids and activated olefins[14—16] (Scheme 1).

Scheme 1



Z = COOMe, CN; X = Br, I

In this work, we studied the one-pot electrocatalytic transformation of malonic acid esters (**1a,b**) and arylidene- or alkylidenemalononitriles (**2a—j**) into esters of 3-substituted 2,2-dicyanocyclopropane-1,1-dicarboxylic acids (**3a—l**). The process was conducted in an undivided cell in methanol or ethanol using NaBr or NaI as a mediator (Scheme 2, Table 1):

Electrolyses of methyl (**1a**) or ethyl (**1b**) malonate in the presence of arylidene- or alkylidenemalononitriles **2a—j** in MeOH or EtOH, respectively, were carried out under direct current in an undivided cell with a graphite

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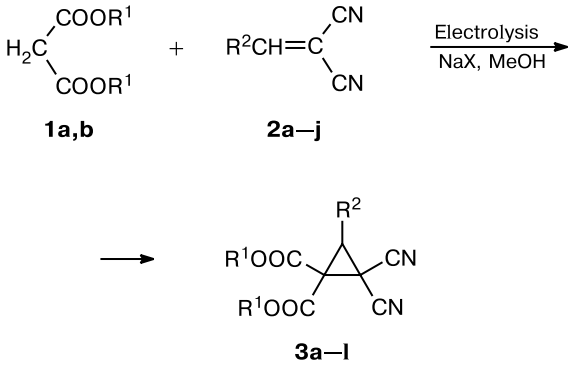
Scheme 2



1: R^1 = Me (**a**), Et (**b**) X = Br, I

2: R^2 = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-$BnOC_6H_4$ (**d**), 2-ClC_6H_4 (**e**), 4-ClC_6H_4 (**f**), 4-$NO_2C_6H_4$ (**g**), Me (**h**), Et (**i**), Pr^n (**j**)

3	R^1	R^2	**3**	R^1	R^2
a	Me	Ph	**g**	Me	2-ClC_6H_4
b	Et	Ph	**h**	Me	4-ClC_6H_4
c	Me	4-MeC_6H_4	**i**	Me	4-$NO_2C_6H_4$
d	Et	4-MeC_6H_4	**j**	Me	Me
e	Me	4-$MeOC_6H_4$	**k**	Me	Et
f	Me	4-$BnOC_6H_4$	**l**	Me	Pr^n

Table 1. Electrocatalytic transformation of dialkyl malonates **1a,b** and arylidene- or alkylidenemalononitriles **2a—j** into cyclopropanes **3a—l** [a]

Ylidenemalononitrile	Dialkyl malonate	*T*/°C	Mediator	Cyclopropane	Yield[b] (%)
2a	**1a**	20	NaBr	**3a**	(31)[c]
	1a	10	NaBr	**3a**	(48)[c]
	1a	0	NaBr	**3a**	75 (87)[c]
	1b	0	NaBr	**3b**	71
	1a	0	NaI	**3a**	63
2b	**1a**	0	NaBr	**3c**	79
	1b	0	NaBr	**3d**	88
2c	**1a**	0	NaBr	**3e**	84
2d	**1a**	0	NaBr	**3f**	79
2e	**1a**	0	NaBr	**3g**	72
2f	**1a**	0	NaBr	**3h**	75
2g	**1a**	0	NaBr	**3i**	58
2h	**1a**	0	NaBr	**3j**	72
	1a	0	NaI	**3j**	61
2i	**1a**	0	NaBr	**3k**	74
2j	**1a**	0	NaBr	**3l**	76

[a] Conditions: 10 mmoles of dialkyl malonate, 10 mmoles of arylidene- or alkylidenemalononitrile, 5 mmoles of mediator, 20 mL of alcohol, Fe cathode, C anode, 1.9 $F\,mol^{-2}$ electricity, current density 100 mA cm^{-2}.

[b] To isolated cyclopropane.

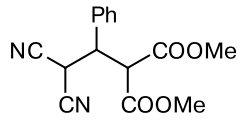
[c] The yields obtained by the data of ^1H NMR spectroscopy are given in parentheses.

anode and iron cathode until the complete conversion of the starting compounds (1.9 $F\,mol^{-1}$).

The optimum temperature for electrolysis is 0 °C. Raising the temperature to 10 °C or 20 °C (the last temperature is optimum for the electrolysis of dialkyl malonate in the presence of alkylidenemalonates[14]) decreases substantially the yield of the corresponding cyclopropane and is accompanied by the formation of considerable amounts of oligomeric compounds. This circumstance impedes the isolation of cyclopropanes **3a—l**.

As in the case of similar reactions of malonic or cyanoacetic acids esters with activated olefins,[14—17] the optimum mediators for the process are salts of hydrobromic acid rather than iodides.

When a smaller quantity of electricity (0.7 $F\,mol^{-1}$) is passed through the reaction of ester **1a** with benzylidenemalononitrile **2a**, dimethyl 3,3-dicyano-2-phenylpropane-1,1-dicarboxylate (**4**) in 25% yield was detected in the reaction mixture by ^1H NMR spectroscopy along with cyclopropane **3a** (32% yield) .



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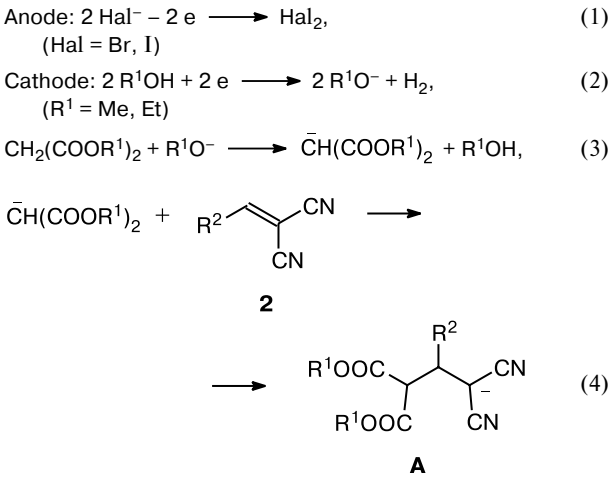
Based on the results of this work and data obtained previously,[14—17] we propose a mechanism of electrocatalytic transformation of malonic acid ester and arylidene- or alkylidenemalononitriles into 3-substituted 2,2-dicyanocyclopropane-1,1-dicarboxylates.

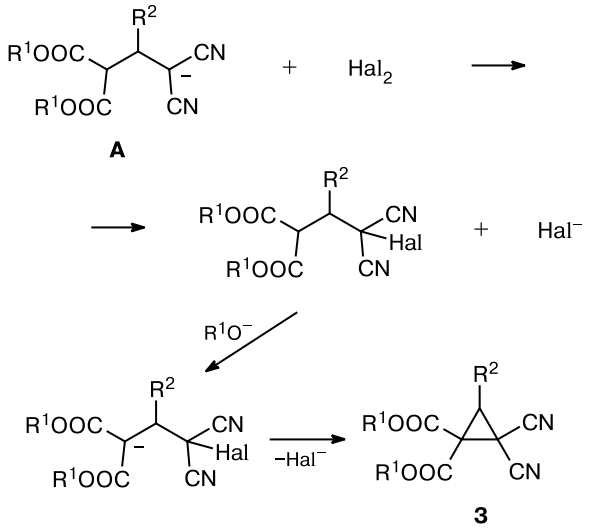
Reactions on electrodes are usual for the mediator system used (halide anion—molecular halogen in alcohols) and include halogen formation on the anode (step 1) and hydrogen evolution on the cathode with the generation of alkoxide ions (step 2) (Scheme 3). In solution, an alkoxide ion interacts with malonic acid ester to form its carboanion (step 3), whose interaction with activated olefin **2** produces anion **A** (step 4).

Scheme 3



The subsequent halogenation of anion **A** and ring closure under the action of the alkoxide ion afford cyclopropane derivative **3** (Scheme 4).

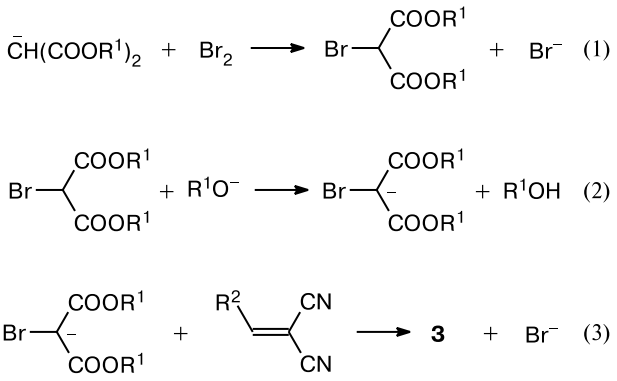
Scheme 4



As found previously,[18] NaI is a more efficient mediator than NaBr for electrocatalytic ring closure of 2-substituted propane-1,1,3,3-tetracarboxylates. This is caused by a higher selectivity of iodine as an oxidant of **A** type anion in the presence of alkoxide ions as compared to bromine. In the electrocatalytic process studied here, NaBr is a more efficient mediator.

This result can be explained by an additional route of the catalytic process (Scheme 5).

Scheme 5



The formation of the bromomalonate anion (see Scheme 5, step 2) from dialkyl malonate during electrolysis in an undivided cell in alcohols in the presence of NaBr has been found earlier.[19] It is known that bromomalonate is a stronger CH-acid than iodomalonate, due to which its deprotonation is faster (see Scheme 5, step 2). In addition, the bromomalonate anion probably adds more rapidly to activated olefin **2** in step 3.

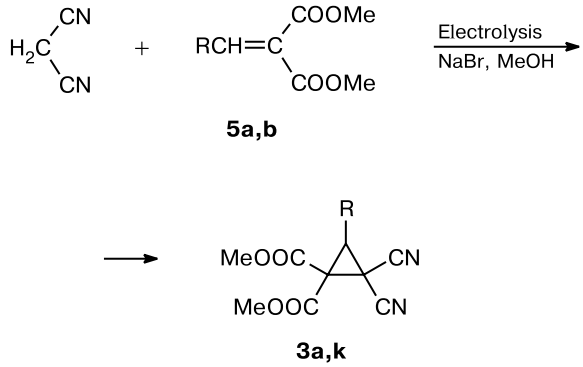
3-Substituted 2,2-dicyanocyclopropane-1,1-dicarboxylates **3a—l** can also be formed when malononitrile and arylidene- or alkylidenemalonic esters are used in electrolysis as the starting substances (see Scheme 6, Table 2).

Table 2. Electrocatalytic transformation of malononitrile and arylidene- or alkylidenemalonic esters into cyclopropanes **3a,k** [a]

Ylidenemalonic ester	R	T/°C	Mediator	Cyclopropane	Yield[b] (%)
5a	Ph	20	NaBr	**3a**	8
5a	Ph	10	NaBr	**3a**	13
5a	Ph	0	NaBr	**3a**	25
5a	Ph	−10	NaBr	**3a**	33
5a	Ph	−20	NaBr	**3a**	46
5a	Ph	−20	NaI	**3a**	35
5b	Et	20	NaBr	**3k**	23
5b	Et	10	NaBr	**3k**	30
5b	Et	0	NaBr	**3k**	42
5b	Et	−10	NaBr	**3k**	53
5b	Et	−20	NaBr	**3k**	67
5b	Et	−20	NaI	**3k**	52

[a] Conditions: 10 mmoles of malononitrile, 10 mmoles of **5a** or **5b**, 5 mmoles of mediator, 20 mL of MeOH, Fe cathode, C anode 1.9 F mol^{-1} electricity, current density 100 mA cm^{-2}.
[b] Data of ^{1}H NMR spectroscopy.

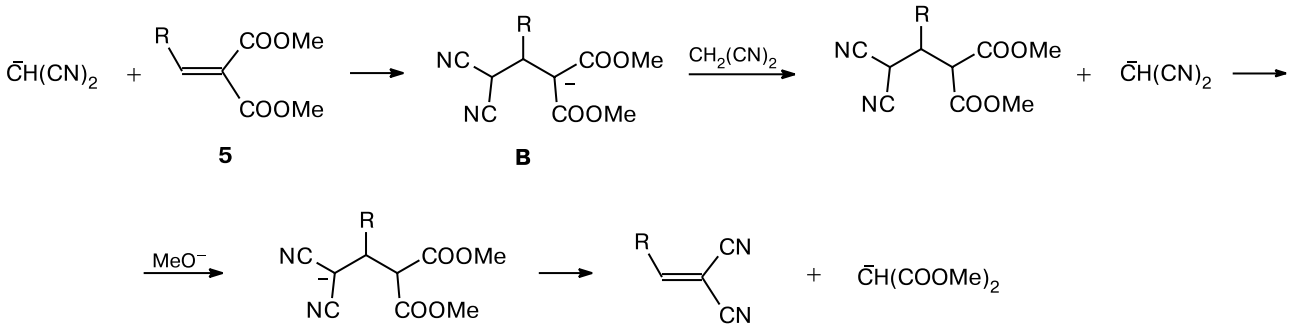
Scheme 6



However, in this case, electrolysis should be carried out (*cf.* Tables 1 and 2) at much lower temperature (−20 °C). Even at this temperature, the yield of cyclic esters **3a,k** (see Table 2) is by 20—40% lower than that in the first case (see Table 1).

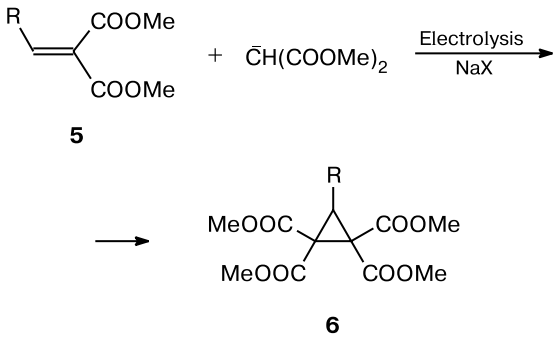
The lower yield of cyclic esters **3** in the second variant (see Table 2) is caused, most likely, by the following factors: (1) enhanced affinity of malononitrile to oligomerization in the presence of bases[20,21]; (2) formation of an intermediate anion (**B**) that interacts with components of the reaction mixture (Scheme 7) and finally decomposes to more stable fragments. Transformations similar to those in Scheme 7 were considered[22] for the reactions of substituted benzylidenemalononitriles with the anion

Scheme 7



of cyanoacetic acid ester. The further transformations of the anion of dialkyl malonate and alkylidenemalonate in the reaction mixture under electrolysis produce cyclic tetraester **6**, due to which the yield of the target dicyanodiester **3** decreases (Scheme 8).

Scheme 8



X = Br, I

For instance, the combined electrolysis of malononitrile and ethylidenemalonate **5b** at temperatures 20, 10, and 0 °C afforded tetraester **6** (21, 15, and 10% yields, respectively) along with dicyano derivative **3k** (23, 30, and 42% yields, respectively), which were detected in the reaction mixtures by ^{1}H NMR spectroscopy and GLC.

Thus, the one-pot combined electrolysis of malonic acid ester and benzylidene- or alkylidenemalononitrile in the presence of a mediator in an undivided cell affords esters of 3-substituted 2,2-dicyanocyclopropane-1,1-dicarboxylic acids in 60—90% yields. Using methods of classical chemistry, this process can be performed rather in two steps: (1) halogenation of malonic acid ester; (2) addition of halomalonic ester to the double bond of arylidene- or alkylidenemalononitrile followed by ring closure in the presence of a base.[23] The procedures for electrolysis and isolation of products are simple and can be used both under laboratory conditions and in larger reactors.

Experimental

^{1}H NMR spectra were obtained on Bruker WM-250 and Bruker AM-300 instruments with working frequencies of 250 and 300 MHz, respectively, in DMSO-d_6 or $CDCl_3$. Chemical shifts in NMR spectra are given in the δ scale relative to Me_4Si.

GLC was carried out on an LKhM-80 chromatograph with a flame-ionization detector (carrier gas nitrogen, flow rate 30 mL min^{-1}, column (glass) 2500×3 mm with 5% SE-Superphase on Inerton Super (0.16—0.20 mm).

Dialkyl malonates and malononitrile are available from Aldrich. Benzylidene- and alkylidenemalononitriles **2a—j** and benzylidene- and ethylidenemalonic acids esters **5a,b** were synthesized by the condensation of the corresponding aldehydes and malononitrile or dialkyl malonates (Merck and Aldrich) *via* the Knoevenagel reaction.[24]

Combined electrolysis of malonic acid ester and arylidene- or alkylidenemalononitriles (general procedure). A solution of dialkyl malonate (**1a**,**b**) (10 mmol), alkylidene- or arylidenemalononitrile (**2a—j**) (10 mmol), and mediator (NaBr or NaI) (5 mmol) in MeOH or EtOH (20 mL) was subjected to electrolysis in an undivided cell equipped with the C anode and Fe cathode (the surface area of the electrodes was 5 cm^2) at a constant current density of 100 mA cm^{-2}, passing a quantity of electricity given in Table 1. After the end of electrolysis, the solution was cooled to −10 °C, and a precipitate of cyclopropane derivative **3** was filtered off and washed with cold alcohol. The mother liquor was concentrated, extracted with $CHCl_3$, washed with water, and dried over Na_2SO_4. The solvent was distilled off, and the resulting residue was recrystallized from an acetone—hexane mixture, which gave an additional amount of product **3**.

Dimethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (3a), m.p. 126—128 °C. Found (%): C, 63.19; H, 4.31, N, 9.67. $C_{15}H_{12}N_2O_4$. Calculated (%): C, 63.38; H, 4.25; N, 9.85. ^{1}H NMR (DMSO-d_6), δ: 3.75, 3.92 (both s, 3 H each, CH_3O); 4.41 (s, 1 H, CH); 7.35—7.50 (m, 5 H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 16.46 (C); 40.24 (CH); 46.36 (C); 53.97 (CH_3O); 54.86 (CH_3O); 109.51, 111.74 (CN); 127.08, 128.62, 129.16, 129.73 (Ar); 161.42, 163.44 (OC=O).

Diethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (3b), m.p. 73—74 °C. Found (%): C, 65.47; H, 5.08; N, 9.07. $C_{17}H_{16}N_2O_4$. Calculated (%): C, 65.38; H, 5.16; N, 8.97. ^{1}H NMR ($CDCl_3$), δ: 1.18, 1.37 (both t, 3 H each, CH_3, J = 7 Hz); 3.97 (s, 1 H, CH); 4.23 (m, 2 H, OCH_2); 4.42 (q, 2 H, OCH_2, J = 7 Hz); 7.30—7.45 (m, 5 H, C_6H_5). ^{13}C NMR

($CDCl_3$), δ: 13.41, 13.77 (both CH_3); 16.15 (C); 39.88 (CH); 46.21 (C); 63.44, 64.30 (both CH_2O); 109.61, 111.77 (both CN); 127.21, 128.62, 128.91, 129.49 (Ar); 160.92, 162.88 (both OC=O).

Dimethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (3c), m.p. 137—139 °C. Found (%): C, 64.31; H, 4.65; N, 9.15. $C_{16}H_{14}N_2O_4$. Calculated (%): C, 64.42; H, 4.73; N, 9.39. ^{1}H NMR ($CDCl_3$), δ: 2.39 (s, 3 H, CH_3); 3.79 (s, 3 H, CH_3O); 3.96 (s, 1 H, CH); 3.98 (s, 3 H, CH_3O); 7.18—7.30 (m, 4 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 16.42 (C); 21.07 (CH_3); 40.14 (CH); 46.27 (C); 53.85, 54.75 (CH_3O); 109.55, 111.75 (CN); 123.89, 128.38, 129.73, 139.76 (Ar); 161.15, 163.44 (OC=O).

Diethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (3d), m.p. 77—79 °C (Ref. 23: m.p. 77 °C). ^{1}H NMR ($CDCl_3$), δ: 1.23, 1.35 (both t, 3 H each, CH_3, J = 7 Hz); 2.37 (s, 3 H, CH_3); 3.72 (s, 1 H, CH); 4.25, 4.38 (both q, 2 H each, CH_2O, J = 7 Hz); 7.20—7.32 (m, 4 H, Ar).

Dimethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (3e), m.p. 108—109 °C. Found (%): C, 61.02; H, 4.55; N, 9.79. $C_{16}H_{14}N_2O_5$. Calculated (%): C, 61.14; H, 4.49; N, 8.91. ^{1}H NMR ($CDCl_3$), δ: 3.78, 3.79 (both s, 3 H each, CH_3O); 3.93 (s, 1 H, CH); 3.94 (s, 3 H, CH_3O); 6.91, 7.27 (both d, 2 H each, Ar, J = 8 Hz). ^{13}C NMR ($CDCl_3$), δ: 16.55 (C); 40.06 (CH); 46.45 (C); 53.81, 54.69, 55.24 (all CH_3O); 109.72, 111.84 (CN); 114.53, 118.80, 129.94, 160.49 (Ar); 161.49, 163.43 (OC=O).

Dimethyl 3-(4-benzyloxyphenyl)-2,2-dicyanocyclopropane-1,1-dicarboxylate (3f), m.p. 147—148 °C. Found (%): C, 67.72; H, 4.53; N, 7.05. $C_{22}H_{18}N_2O_5$. Calculated (%): C, 67.69; H, 4.65; N, 7.18. ^{1}H NMR ($CDCl_3$), δ: 3.79 (s, 3 H, CH_3O); 3.94 (s, 1 H, CH); 3.99 (s, 3 H, CH_3O); 5.08 (s, OCH_2); 7.01, 7.28 (both d, 2 H each, Ar, J = 8 Hz); 7.30—7.50 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 16.56 (C); 40.04 (CH); 46.33 (C); 53.98, 54.86 (both CH_3O); 69.98 (CH_2O); 109.68, 111.75 (CN); 115,36, 118.91, 127.01, 127.47, 128.14, 128.59, 129.98, 136.18, 159.61 (Ar); 161.50, 163.45 (OC=O).

Dimethyl 3-(2-chlorophenyl)-2,2-dicyanocyclopropane-1,1-dicarboxylate (3g), m.p. 116—117 °C. Found (%): C, 56.37; H, 3.45, Cl, 10.98; N, 8.57. $C_{15}H_{11}ClN_2O_4$. Calculated (%): C, 56.53; H, 3.48; Cl, 11,12; N, 8.79. ^{1}H NMR ($CDCl_3$), δ: 3.81 (s, 3 H, CH_3O); 3.96 (s, 1 H, CH); 3.99 (s, 3 H, CH_3O); 7.25—7.55 (m, 4 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 17.10 (C); 39.11 (CH); 46.18 (C); 54.05, 54.81 (CH_3O); 109.27, 111.63 (CN); 125.80, 127.22, 129.09, 130.22, 130.94, 135.56 (Ar); 161.52, 163.17 (OC=O).

Dimethyl 3-(4-chlorophenyl)-2,2-dicyanocyclopropane-1,1-dicarboxylate (3h), m.p. 108—110 °C. Found (%): C, 56.29; H, 3.58, Cl, 11.25; N, 8.63. $C_{15}H_{11}ClN_2O_4$. Calculated (%): C, 56.53; H, 3.48; Cl, 11,12; N, 8.79. ^{1}H NMR ($CDCl_3$), δ: 3.79 (s, 3 H, CH_3O); 3.92 (s, 1 H, CH); 3.98 (s, 3 H, CH_3O); 7.25—7.45 (m, 4 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 16.45 (C); 39.50 (CH); 46.29 (C); 54.13, 55.00 (CH_3O); 109.36, 111.45 (CN); 125.57, 129.47, 129.73, 139.76 (Ar); 161.23, 163.25 (OC=O).

Dimethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (3i), m.p. 140—142 °C. Found (%): C, 54.57; H, 3.28; N, 12.65. $C_{15}H_{11}N_3O_6$. Calculated (%): C, 54.72; H, 3.37; N, 12.76. ^{1}H NMR ($CDCl_3$), δ: 3.85, 4.02 (both s, 3 H each, CH_3O); 4.05 (s, 1 H, CH); 7.62, 8.31 (both d, 2 H each, J = 7 Hz). ^{13}C NMR ($CDCl_3$), δ: 16.44 (C); 39.17 (CH); 46.23 (C); 54.38, 55.22 (CH_3O); 109.13, 111.19 (CN); 124.27, 130.07, 134.00, 134.06 (Ar); 161.13, 163.11 (OC=O).

Dimethyl 2,2-dicyano-3-methylcyclopropane-1,1-dicarboxylate (3j), m.p. 88—89 °C. Found (%): C, 53.93; H, 4.58; N, 12.43. $C_{10}H_{10}N_2O_4$. Calculated (%): C, 54.05; H, 4.54; N, 12.61. ^{1}H NMR ($CDCl_3$), δ: 1.49 (d, 3 H, CH_3, J = 7 Hz); 2.79 (q, 1 H, CH, J = 7 Hz); 3.92 (s, 6 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 10.82 (CH_3); 16.32 (C); 32.77 (CH); 45.65 (C); 53.97, 54.55 (CH_3O); 109.98, 111.32 (CN); 161.62, 163.55 (OC=O).

Dimethyl 2,2-dicyano-3-ethylcyclopropane-1,1-dicarboxylate (3k), m.p. 43—45 °C. Found (%): C, 55.75; H, 4.98, N, 12.01. $C_{11}H_{12}N_2O_4$. Calculated (%): C, 55.93; H, 5.12; N, 11.86. ^{1}H NMR ($CDCl_3$), δ: 1.21 (t, 3 H, CH_3, J = 7 Hz); 1.64, 1.82 (both m, 1 H each, CH); 2.65 (t, 1 H, CH, J = 7 Hz); 3.91 (s, 6 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 11.87 (CH_3); 15.47 (C); 19.91 (CH_2); 38.99 (CH); 45.72 (C); 53.98, 54.57 (CH_3O); 109.98, 111.41 (CN); 161.68, 163.57 (OC=O).

Dimethyl 2,2-dicyano-3-propylcyclopropane-1,1-dicarboxylate (3l), m.p. 62—64 °C. Found (%): C, 57.43; H, 5.58; N, 11.13. $C_{12}H_{14}N_2O_4$. Calculated (%): C, 57.59; H, 5.64; N, 11.19. ^{1}H NMR ($CDCl_3$), δ: 1.03 (t, 3 H, CH_3, J = 7 Hz); 1.52—1.88 (m, 4 H, CH_2); 2.68 (t, 1 H, CH, J = 7 Hz); 3.91 (s, 6 H, CH_3O). ^{13}C NMR ($CDCl_3$), δ: 13.50 (CH_3); 15.69 (C); 20.93, 27.91 (CH_2); 37.56 (CH); 45.46 (C); 54.01, 54.61 (CH_3O); 110.08, 111.44 (CN); 161.74, 163.63 (OC=O).

Dimethyl 3,3-dicyano-2-phenylpropane-1,1-dicarboxylate (4) was synthesized by the reaction of benzylidenemalononitrile (10 mmol, 1.54 g) with dimethyl malonate (10 mmol, 1.32 g) in MeOH (10 mL) in the presence of sodium methoxide (1 mmol), which was prepared by the dissolution of Na (0.023 g) in MeOH. The reaction mixture was stirred for 1 h, and a precipitate formed was filtered off. An additional amount of ester **4** was obtained by concentrating of the mother liquor followed by crystallization of the residue from MeOH. Ester **4** was obtained in 63% yield (1.82 g), m.p. 86—87 °C. Found (%): C, 62.78; H, 4.79; N, 9.63. $C_{15}H_{14}N_2O_4$. Calculated (%): C, 62.93; H, 4.93; N, 9.79. ^{1}H NMR ($CDCl_3$), δ: 3.50, 3.86 (both s, 3 H each, CH_3O); 3.95 (dd, 1 H, CH, J_1 = 12 Hz, J_2 = 7 Hz); 4.14 (d, 1 H, CH, J = 12 Hz); 4.90 (d, 1 H, CH, J = 7 Hz); 7.42 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 27.53, 44.55 (both CH); 52.86 (CH_3O); 53.08 (CH); 53.43 (CH_3O); 111.26, 111.31 (CN); 128.26, 129.07, 129.46, 133.48 (Ar); 166.21, 167.63 (OC=O).

Tetramethyl 3-ethylcyclopropane-1,1,2,2-tetracarboxylate (6) was synthesized by a known procedure,[14], m.p. 58—59 °C (Ref. 25: m.p. 59—60 °C). ^{1}H NMR ($CDCl_3$), δ: 1.02 (t, 3 H, CH_3, J = 7 Hz); 1.83 (m, 2 H, CH_2); 2.38 (t, 1 H, CH, J = 7 Hz); 3.74, 3.75 (both s, 6 H each, OCH_3).

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