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Electrochemical Transformation of Malononitrile and Carbonyl Compounds into Functionally Substituted Cyclopropanes: Electrocatalytic Variant of the Wideqvist Reaction

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Abstract—Electrolysis of malononitrile and carbonyl compounds in the presence of alkali metal halides in an undivided cell results in the formation of substituted 1,1,2,2-tetracyanocyclopropanes in 60–90% yield. This electrocatalytic variant of the Wideqvist reaction using malononitrile instead of bromomalonitrile was successfully performed. Electrocatalytic transformation of substituted 1,1,2,2-tetracyanocyclopropanes in methanol or ethanol in an undivided cell leads to substituted 2-amino-4,4-dialkoxy-1,5-dicyano-3-azabicyclo[3.1.0]hex-2-enes in 70–95% yields after 0.05–0.10 F/mol of electricity has been passed.

Malononitrile is one of the most famous and useful reagents for the synthesis of heterocyclic compounds, pharmaceuticals, pesticides, fungicides, solvatochromic dyes, and charge-transfer salts. The unique reactivity of this compound has led to its widespread application in organic chemistry, as well as or even more than other CH acids—malonate and cyanoacetic esters.

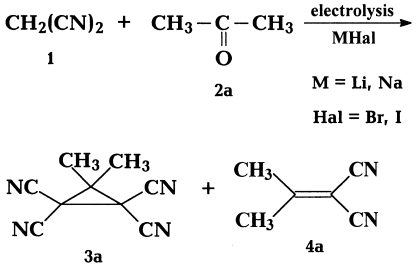
Nevertheless, little is known about the electrochemistry of malononitrile. Although the first electrochemical oxidation of malonate anion was performed in the 19th century,[1] electrooxidation, electroreduction, or any other electrochemical transformations of malononitrile are not mentioned in books or reviews of electroorganic chemistry,[2–5] nor in reviews dealing with the application of malononitrile in organic synthesis.[6,7] To our knowledge, apart from the work of our research group, there is only one publication which is concerned with this problem and describes the electrochemical anodic arylation of malononitrile.[8]

In the last few years, mediators were widely used for the electrooxidation and electroreduction of organic compounds.[5] Among a variety of mediators, the redox system halide anion—halogen is one of the most useful from the viewpoint of organic synthesis and large-scale processes.[9]

Recently, in the course of our study on the electrochemical oxidation of organic compounds in the presence of alkali metal halides, we have carried out the electrochemical transformation of cyanoacetic ester and aldehydes into 3-substituted 1,2-dicyanocyclopropane-1,2-dicarboxylates[10] as well as malonitrile and ketones into substituted 1,1,2,2-tetracyanocyclopropanes.[11] The present paper is devoted to a detailed study of the co-electrolysis of malononitrile and carbonyl compounds in order to estimate the scope and limitations of the synthetic utility of this process.

Electrolysis of malononitrile **1** in acetone in the presence of alkali metal halides as mediators was carried out in an undivided cell with a Pt-anode and an Fe-cathode under constant current density. Under these conditions, malononitrile and acetone were transformed into 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane **3a** and isopropylidenemalononitrile **4a** (Table 1, Scheme 1).

It has been found that bromides are more effective mediators than iodides. With sodium iodide as mediator, the yield of cyclopropane **3a** decreased by 30% and the main route of the process in this case became the formation of alkene **4a**. The reaction can also be accomplished as co-electrolysis of



Scheme 1.

Keywords: electrochemical reaction; catalysis; cyclopropanes; ketones.

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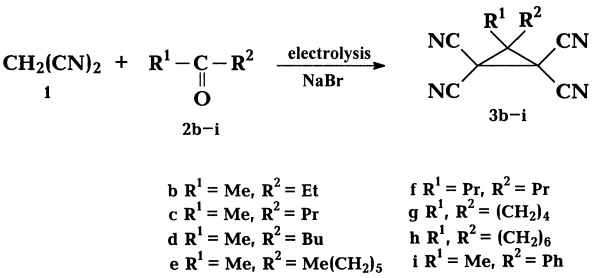
Table 1. Electrochemical reaction of malononitrile with acetone (30 mmol of **1**, 8 mmol of mediator, Pt-anode, Fe-cathode, current density 200 mA/cm^2, 20°C, electricity passed 1 F/mol of **1**)

Mediator (electrolyte)	Acetone (ml)	Ethanol (ml)	Conversion of **1** [%]	Yield of **3a**		Yield of **4a**	
				Substance yield (%)[a]	Current yield (%)	Substance yield (%)[b]	Current yield (%)
NaI	20	–	83	18	15	42	35
NaBr	20	–	84	48	40	35	29
LiBr	20	–	81	45	36	31	25
NaBr	10	10	95	61	58	29	28
NaBr	5	15	98	72	71	18	18
NaBr	3	17	100	56	56	15	15
NaBr	5	15[c]	99	46	46	27	27
NaBr	5	15[d]	84	14	12	35	29

[a] Isolated yields, based on **1** consumed.
[b] Determined by NMR spectroscopy.
[c] MeOH as a co-solvent.
[d] MeCN as a co-solvent.



Scheme 2.

malonitrile **1** and acetone in ethanol, methanol, or acetonitrile as a solvent. Ethanol was found to be the optimal solvent. For reaction carried out in ethanol, the yield of **3a** depends on the concentration of acetone in the reaction mixture. The optimum yield of **3a** was achieved when 25% by volume concentration of acetone was used.

Table 2. Electrochemical reactions of malononitrile with ketones (30 mmol of **1**, 5 ml of ketone, 8 mmol of NaBr in 15 ml of EtOH, Pt-anode, Fe-cathode, current density 200 mA/cm^2, 20°C, electricity passed 1.2 F/mol of ketone)

Ketone	R^1	R^2	Cyclopropanes **3b–i**	
			Substance yield (%)[a]	Current yield (%)
2b	Me	Et	91	76
2c	Me	Pr	75	63
2d	Me	Bu	71	59
2e	Me	$(CH_2)_5Me$	70	58
2f	Pr	Pr	32	27
2g		$(CH_2)_4$	86	72
2h		$(CH_2)_6$	60	50
2i	Ph	Me	25	21

[a] Isolated yields.

The similar electrolysis of malononitrile in the presence of ketones **2b–i** was carried out under the same conditions, which were optimised for the transformation of malononitrile and acetone into cyclopropane **3a** (Table 2, Scheme 2).

Surprisingly, under the same conditions, the reaction of malononitrile and cyclohexanone led to 2-amino-1,5-dicyano-4,4-diethoxy-6,6-pentamethylene-3-azabicyclo[3.1.0]-hex-2-ene **5a** in 62% yield (Scheme 3).

The electrolysis of malononitrile in the presence of aldehydes also results in the formation of 1,1,2,2-tetracyanocyclopropanes (Table 3, Scheme 4).

In the case of aldehydes it is not necessary to use an excess of the carbonyl compound. Decreasing the temperature of electrolysis from 20 to 0°C ensures the formation of **6a–h** in high yields. Further decreasing the temperature or using an excess of aldehyde in this reaction leads to the formation of alkylidenemalononitriles $RCH{=}C(CN)_2$ in substantial yields (up to 40% at −20°C).

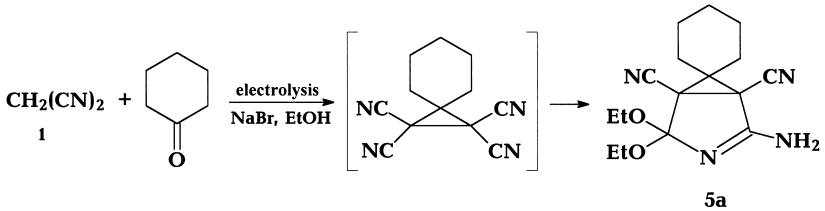
Discussion

Taking into consideration the above results, the following general mechanism of the electrochemical transformation of malononitrile and carbonyl compounds into substituted 1,1,2,2-tetracyanocyclopropanes is suggested.

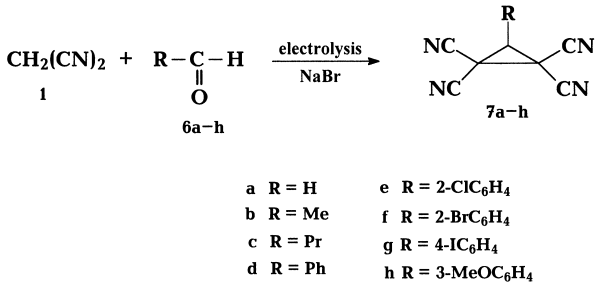
The reactions at the electrodes, which take place during the process, are shown below:

anode : $2Hal^- - 2e \rightarrow Hal_2$ $\quad Hal = Br, I$

cathode : $2CH_2(CN)_2 + 2e \rightarrow \bar{C}H(CN)_2 + H_2$



Scheme 3.



Scheme 4.

The formation of iodine or bromine at the anode is a well-known process and the corresponding colour is observed when the electrolysis is conducted without stirring the reaction mixture.

The alternative reaction on the cathode when ethanol or methanol is used as solvent or co-solvent could be the formation of alkoxide ion on the cathode. However, in this case, the following reaction in solution between alkoxide ion and malononitrile should lead to the formation of malononitrile ion as the general result of the cathodic process.

The reaction of malononitrile anion with carbonyl compounds leading to alkylidenemalonates has been studied earlier:[12]

$$\bar{C}H(CN)_2 + R^1R^2CH{=}O \rightarrow R^1R^2C{=}C(CN)_2 + HO^-$$

The bromination of malononitrile anion by halogen generated at the anode, the formation of halogenomalononitrile anion, followed by addition of the latter to alkylidenemalonate gives rise to substituted 1,1,2,2-tetracyanocyclopropane:

$$\bar{C}H(CN)_2 + Hal_2 \rightarrow CH(Hal)(CN)_2 + Hal^- \quad (1)$$

$$CH(Hal)(CN)_2 + HO^- \rightarrow \bar{C}Hal(CN)_2 + H_2O \quad (2)$$

$$\bar{C}Hal(CN)_2 + R^1R^2C{=}C(CN)_2 \longrightarrow \text{(tetracyanocyclopropane)} + Hal^- \quad (3)$$

Sodium bromide is more effective as a mediator for the above process than sodium iodide. This result is directly related to the fact that intermediate bromomalononitrile is a stronger CH acid than iodomalononitrile and thus the stage of proton abstraction with the formation of halogenomalononitrile anion **(2)** is faster in the case of sodium bromide as a mediator.

The maximum yield of **3a** was achieved under the conditions with 25% by volume concentration of acetone. When the higher concentration of acetone is used, the larger quantity of isopropylidenemalononitrile **4a** is obtained at the end of the electrolysis.

Tetracyanocyclopropanes **3f** and **3i** were obtained in lower yields (32 and 25%, respectively) than those in all other cases. This is related to a lower rate of the reaction of the corresponding ketones **2f** and **2i** with malononitrile, and in these two cases a side reaction is the oligomerisation of malononitrile under the conditions of the electrolysis.

However, there is a possibility of increasing the yield of **3f** and **3i** by performing the electrolysis of alkylidenemalonates in the presence of malononitrile (Scheme 5).

The results in Table 4 also confirm the suggested mechanism.

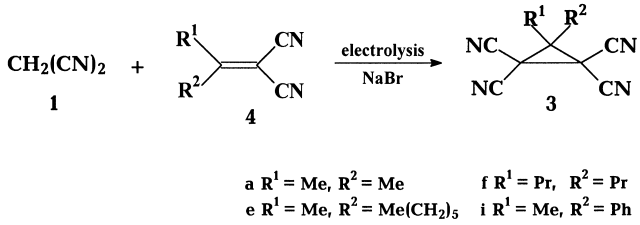
In the case of the electrochemical reaction of cyclohexanone with malononitrile in EtOH, the corresponding tetracyanocyclopropane is very easily attacked by ethoxide anion and affords the further transformation into bicyclic pyrroline **5a**.

It has been found that the above process is a general reaction for tetracyanocyclopropanes (Scheme 6).

Table 3. Electrochemical reactions of malononitrile with aldehydes (20 mmol of **1**, 20 mmol of aldehyde, 8 mmol of NaBr in 20 ml of EtOH, Pt-anode, Fe-cathode, current density 100 mA/cm^2, 0°C)

Aldehyde	R^1	Electricity passed (F/mol)	Cyclopropanes **7a–h**: substance yield, (%)[a]
6a	H	1.8	60
6b	Me	1.2	65
6c	Pr	1.4	76
6d	Ph	1.2	78
6e	2-ClC_6H_4	1.8	95
6f	2-BrC_6H_4	1.7	76
6g	4-IC_6H_4	1.2	96
6h	3-$MeOC_6H_4$	1.2	90

[a] Isolated yields.

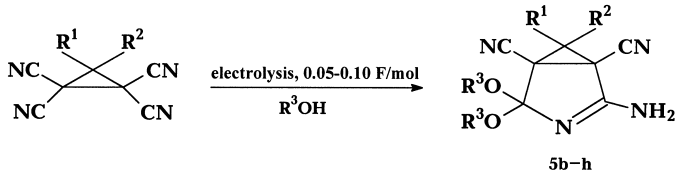


Scheme 5.

Table 4. Electrochemical reactions of malononitrile with alkylidenemalononitriles (20 mmol of **1**, 20 mmol of alkylidenemalononitrile **4**, 8 mmol of NaBr in 20 ml of EtOH, Pt-anode, Fe-cathode, current density 200 mA/cm^2, 20°C, electricity passed 1.2 F/mol)

Alkylidene-malononitrile	R^1	R^2	Cyclopropanes **3**	
			Substance yield (%)[a]	Current yield (%)
4a	Me	Me	82	68
4e	Me	$Me(CH_2)_5$	78	65
4f	Pr	Pr	75	63
4i	Me	Ph	62	52

[a] Isolated yields.



Scheme 6.

Table 5. Electrocatalytic transformation of 1,1,2,2-tetracyanocyclopropanes into 2-amino-4,4-dialkoxy-1,5-dicyano-3-azabicyclo[3.1.0]hex-2-enes (6 mmol of substrate, 8 mmol of NaBr in 20 ml of R^3OH, Pt-anode, Fe-cathode, current density 200 mA/cm^2, 20°C, reaction time 1–2 min)

Substrate	R^1	R^2	R^3	Electricity passed (F/mol)	Product, yield (%)[a]
3a	Me	Me	Me	0.1	**5b**, 94
3a	Me	Me	Et	0.1	**5c**, 95
3b	Et	Me	Me	0.05	**5d**, 93
6c	Pr	H	Me	0.1	**5e**, 80
3c	Pr	Me	Me	0.1	**5f**, 71
6d	Ph	H	Et	0.1	**5g**, 81
3g	$(CH_2)_4$		Me	0.1	**5h**, 95

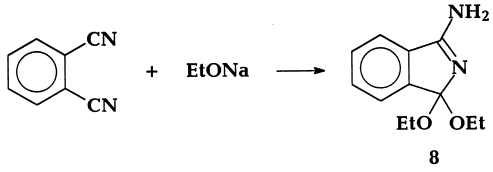
[a] Isolated yields.

The R^3O^- ion generated at cathode reacts with **3a–c,g** or **6c**,**d** forming **5b–h**; complete conversion of the substrate was achieved when only 0.05–0.01 F/mol of electricity was passed (current yield 700–1800%).

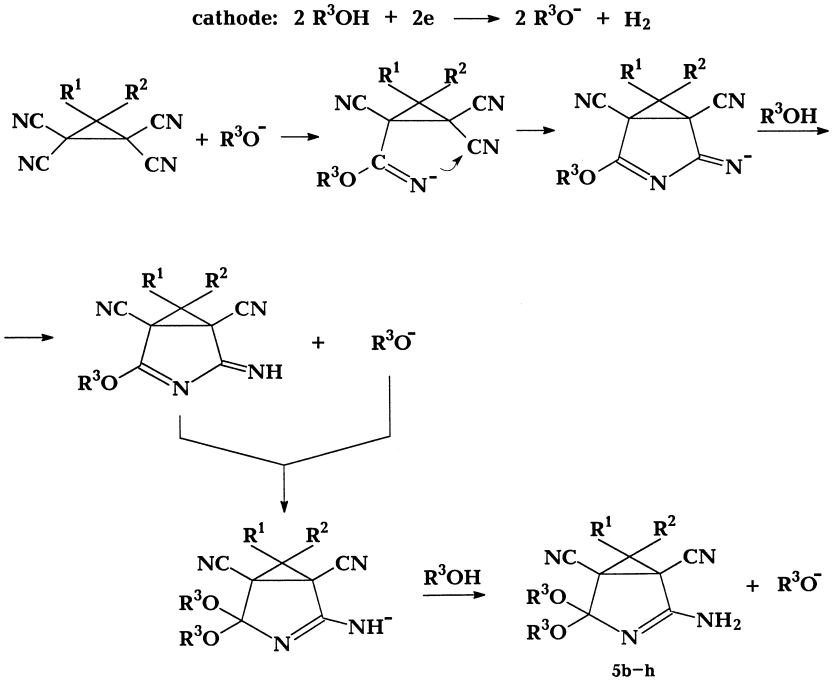
The suggested mechanism of the reaction involves the steps shown in Scheme 7.

The formation of **5b–h** as a result of the chain electrocatalytic mechanism shown in Scheme 7 takes place by successive addition of two R^3OH molecules to the initial tetracyanocyclopropane initiated by R^3O^- ion and includes the regeneration of R^3O^- anion at the last stage, which continues the chain reaction process by the interaction with the next molecule of tetracyanocyclopropane.

The only analogue of this reaction known to us is that between phthalonitrile and EtONa, which gives isoindole derivative **8**.[13]



Thus, the simple electrocatalytic system can produce under mild conditions direct 'one-pot' transformations of malononitrile and carbonyl compounds into the corresponding substituted tetracyanocyclopropanes in high yields. Under similar electrocatalytic conditions, tetracyanocyclopropanes were transformed into corresponding bicyclic pyrrolines **5b–h**. These processes are economical and convenient methods for the electrochemical synthesis of tetracyanocyclopropanes and bicyclic pyrrolines, using only inexpensive reagents and simple equipment; they are easily carried out in an undivided cell.



Scheme 7.

Experimental

GLC analyses were carried out on an 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 in $CDCl_3$ on a Bruker WM-250 (250 MHz) or a Bruker AM-300 (300 MHz) spectrometer, with tetramethylsilane (TMS) as the internal standard.

General electrolysis procedure for the reaction of malononitrile with ketones

A solution of **1** (30 mmol), sodium halide (8 mmol), and ketone (3–5 ml) in 15 ml of ethanol was electrolysed in an undivided cell equipped with a Pt-anode and an Fe-cathode at 20°C under constant current density 200 mA/cm^2 until the quantity of the electricity indicated in Tables 1 and 2 (1 or 1.2 F/mol) was passed. The solvent and an excess of ketone were removed, and the residue was extracted with ethyl acetate, washed with water, and dried with Na_2SO_4. Ethyl acetate was then removed, and the residue was crystallised from acetone–hexane.

1,1,2,2-Tetracyano-3,3-dimethylcyclopropane (3a).[14,15] Mp 210–211°C (Lit.[14] 209.5–210°C), ^{1}H NMR (DMSO-d_6): δ 1.57 s. ^{13}C NMR (acetone-d_6): δ 19.82 q, 27.91 s, 41.52 s, 110.63 s.

1,1,2,2-Tetracyano-3-ethyl-3-methylcyclopropane (3b).[15,16] Mp 208–209°C (Lit.[15] 204–206°C), ^{1}H NMR (acetone-d_6): δ 1.32 (t, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.15 (q, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ 8.91 q, 15.93 q, 26.42 t, 27.43 s, 44.51 s, 110.12 s.

1,1,2,2-Tetracyano-3-methyl-3-propylcyclopropane (3c).[15,17] Mp 170–171°C (Lit.[17] 167.5–168°C), ^{1}H NMR (DMSO-d_6): δ 0.95 (t, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.60–1.90 (m, 4H, CH_2). ^{13}C NMR (acetone-d_6): δ 14.01 q, 17.13 q, 19.11 t, 27.83 s, 39.91 t, 44.52 s, 110.31 s.

3-Butyl-1,1,2,2-tetracyano-3-methylcyclopropane (3d). Mp 130–132°C, ^{1}H NMR (acetone-d_6): δ 0.95 (t, 3H, CH_3), 1.45 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.81 (s, 3H, CH_3), 2.15 (t, 2H, CH_2). ^{13}C NMR (acetone-d_6): δ 13.92 q, 17.21 q, 23.13 t, 27.72 t, 28.01 s, 33.94 t, 44.71 s, 110.43 s. Anal. calcd for $C_{12}H_{12}N_4$: C, 67.92; H, 5.66; N 26.42. Found: C, 67.86; H, 5.79; N 26.67.

1,1,2,2-Tetracyano-3-hexyl-3-methylcyclopropane (3e). Mp 78–80°C (Lit.[16] 80–80.5°C), ^{1}H NMR (acetone-d_6): δ 0.90 (t, 3H, CH_3), 1.40–1.65 (m, 8H, CH_2), 1.75 (s, 3H, CH_3), 2.11 (t, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ 13.61 q, 17.43 q, 21.72 t, 24.04 t, 27.32 s, 28.31 t, 30.72 t, 32.71 t, 43.72 s, 109.72 s, 109.81 s.

1,1,2,2-Tetracyano-3,3-dipropylcyclopropane (3f). Mp 122–123°C, ^{1}H NMR (acetone-d_6): δ 0.95 (t, 6H, CH_3), 1.50–1.85 (m, 8H, CH_2). ^{13}C NMR (acetone-d_6): δ 13.91 q, 19.03 t, 27.61 s, 32.83 t, 47.52 s, 110.41 s. Anal. calcd for $C_{13}H_{14}N_4$: C, 69.03; H, 6.19; N 24.78. Found: C, 68.78; H, 6.07; N 25.01.

1,1,2,2-Tetracyano-3,3-tetramethylenecyclopropane (3g).[15,17] Mp 250–251°C (Lit.[15] 240–243°C), ^{1}H NMR (CD_3OD): δ 1.10 (m, 4H, CH_2) 1.72 (m, 4H, CH_2). ^{13}C NMR (acetone-d_6): δ 27.12 t, 27.91 s, 33.23 t, 51.11 s 110.50 s. Anal. calcd for $C_{11}H_8N_4$: C, 67.35; H, 4.08; N 28.57. Found: C, 67.56; H, 4.02; N 28.82.

1,1,2,2-Tetracyano-3,3-hexamethylenecyclopropane (3h). Mp 170–171°C, ^{1}H NMR ($CDCl_3$): δ 1.80–2.00 (m, 8H, CH_2), 2.17 (m, 4H, CH_2). ^{13}C NMR (DMSO-d_6): δ 22.71 t, 27.43 t, 28.11 s, 32.23 t, 47.42 s 119.91 s. Anal. calcd for $C_{13}H_{12}N_4$: C, 69.64; H, 5.36; N 25.01. Found: C, 69.93; H, 5.17; N 24.97.

1,1,2,2-Tetracyano-3-methyl-3-phenylcyclopropane (3i). Mp 254–255°C (Lit.[16] 225°C), ^{1}H NMR (acetone-d_6): δ 1.91 (s, 3H, CH_3), 7.40–7.80 (m, 5H, C_6H_5). ^{13}C NMR (DMSO-d_6): δ 23.41 q, 27.93 s, 47.62 s 109.93 s, 110.21 s, 128.92 d, 129.31 d, 129.83 d, 132.51 s.

Isopropylidene malonitrile (4a). The compound **4a** was isolated by distillation of the rest of reaction mixture of the electrolysis of malononitrile in acetone in the presence of NaI as mediator (Table 1) after isolation of **3a** in 18% yield, bp 106–108°C (21 Torr), n_D^{25} 1.4663 (Lit.[15] n_D^{23} 1.4670), ^{1}H NMR ($CDCl_3$): δ 2.23 s.

2-Amino-1,5-dicyano-4,4-diethoxy-6,6-pentamethylene-3-azabicyclo[3.1.0]hex-2-ene 5a. Mp 155–157°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 1.15 (t, 6H, CH_2), 1.40–1.95 (m, 10H, CH_2), 3.40–3.75 (m, 4H, CH_2O), 7.40 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 14.81 q, 15.23 q, 23.92 t, 24.41 t, 24.72 t, 25.63 t, 31.81 t, 39.32 s, 41.81 s, 44.82 s, 57.03 t, 59.21 t, 113.52 s, 114.43 s, 116.21 s, 156.52 s. Anal. calcd for $C_{16}H_{22}N_4O_2$: C, 63.58; H, 7.28; N 18.54. Found: C, 63.45; H, 7.14; N 18.38.

General electrolysis procedure for the reaction of malononitrile with aldehydes

A solution of **1** (20 mmol), aldehyde (20 mmol), and sodium bromide (8 mmol) in 20 ml of ethanol was electrolysed in an undivided cell equipped with a Pt-anode and an Fe-cathode at 0°C under constant current density 100 mA/cm^2 until the quantity of the electricity indicated in Table 3 was passed. The solvent was removed, and the residue was extracted with ethyl acetate, washed with water, and dried with Na_2SO_4. Ethyl acetate was removed, and the residue was crystallised from ethyl acetate–hexane.

1,1,2,2-Tetracyanocyclopropane (7a).[18,19] Mp 230–232°C (decomp.) [Lit.[18] 223–225°C (decomp.)], ^{1}H NMR (DMSO-d_6): δ 3.55 s. ^{13}C NMR (DMSO-d_6): δ 17.71 s, 28.83 t, 110.91 s.

1,1,2,2-Tetracyano-3-methylcyclopropane (7b).[16,20] Mp 189–191°C (Lit.[20] 192°C), ^{1}H NMR (DMSO-d_6): δ 1.49 (d, 3H, CH_3), 3.66 (q, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 11.62 q, 22.81 s, 35.93 d, 109.52 s, 110.91 s.

1,1,2,2-Tetracyano-3-propylcyclopropane (7c).[17,20] Mp 136–138°C (Lit.[20] 131°C), ^{1}H NMR (DMSO-d_6): δ 0.95 (t, 3H, CH_3), 1.58 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 3.86

(t, 1H, CH). ^{13}C NMR (DMSO-d_6): δ 13.21 q, 19.33 t, 28.62 t, 22.11 s, 39.23 d, 109.41 s, 110.73 s.

1,1,2,2-Tetracyano-3-phenylcyclopropane (7d).[16,21] Mp 229–231°C (Lit.[21] 227–230°C), ^{1}H NMR (DMSO-d_6): δ 5.10 (s, 1H, CH), 7.48–7.80 (m, 5H, C_6H_5). ^{13}C NMR (DMSO-d_6): δ 23.02 s, 41.93 d, 109.32 s, 110.91 s, 126.81 d, 128.93 d, 129.52 d, 130.01 s.

3-(2-Chlorophenyl)-1,1,2,2-tetracyanocyclopropane (7e). Mp 246–247°C (decomp.) (Lit.[21] 246–248°C), ^{1}H NMR (DMSO-d_6): δ 5.22 (s, 1H, CH), 7.50–8.15 (m, 4H, Ar). ^{13}C NMR (DMSO-d_6): δ 23.52 s, 40.41 d, 109.24 s, 110.51 s, 125.02 d, 127.81 d, 130.13 d, 131.23 d, 132.11 s, 134.13 s.

3-(2-Bromophenyl)-1,1,2,2-tetracyanocyclopropane (7f). Mp 248–249°C (decomp.) (Lit.[21] 249–252°C), ^{1}H NMR (DMSO-d_6): δ 5.48 (s, 1H, CH), 7.40–8.10 (m, 4H, Ar). ^{13}C NMR (DMSO-d_6): δ 23.51 s, 40.42 d, 109.21 s, 110.52 s, 125.03 d, 127.82 d, 130.11 d, 131.22 d, 132.13 s, 134.01 s.

1,1,2,2-Tetracyano-3-(4-iodophenyl)cyclopropane (7g). Mp 227–229°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 5.28 (s, 1H, CH), 7.65 (d, 2H, Ar), 7.89 (d, 2H, Ar). ^{13}C NMR (DMSO-d_6): δ 23.11 s, 41.32 d, 97.53 s, 109.41 s, 110.82 s, 126.73 d, 131.72 d, 137.71 s. Anal. calcd for $C_{13}H_5N_4I$: C, 45.35; H, 1.45; N, 16.28; I, 36.92. Found: C, 45.71; H, 1.54; N, 16.36; I, 36.85.

1,1,2,2-Tetracyano-3-(3-methoxyphenyl)cyclopropane (7h). Mp 227–229°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 3.76 (s, 3H, OCH_3), 5.28 (s, 1H, CH), 6.90–7.70 (m, 4H, Ar). ^{13}C NMR (DMSO-d_6): δ 23.12 s, 41.72 d, 55.53 q, 109.41 s, 110.92 s, 115.13 s, 115.82 d, 121.41 d, 128.13 d, 130.11 d, 149.43 s. Anal. calcd for $C_{14}H_8N_4O$: C, 67.74; H, 3.23; N, 22.58. Found: C, 67.89; H, 3.14; N, 22.63.

General electrolysis procedure for the reaction of malononitrile with alkylidenemalononitriles

A solution of **1** (20 mmol), alkylidenemalononitrile (20 mmol), and sodium bromide (8 mmol) in 20 ml of ethanol was electrolysed in an undivided cell equipped with a Pt-anode and an Fe-cathode at 20°C under constant current density 200 mA/cm^2 until the quantity of the electricity indicated in Table 4 was passed (1.2 F/mol). The solvent was removed, and the residue was extracted with ethyl acetate, washed with water, and dried with Na_2SO_4. Ethyl acetate was then removed, and the residue was crystallised from acetone–hexane.

General electrolysis procedure for the conversion of tetracyanocyclopropanes into substituted bicyclic pyrrolines

A solution of tetracyanocyclopropane (6 mmol) and sodium bromide or sodium acetate (8 mmol) in 20 ml of alcohol was electrolysed in an undivided cell equipped with a Pt-anode and an Fe-cathode at 20°C under constant current density 100 mA/cm^2 until the quantity of the electricity indicated in Table 5 was passed (0.05–0.10 F/mol). Usually bicyclic pyrrolines were crystallised directly from the reaction mixture and were then filtered off. In other cases, the solvent was removed, and the residue was extracted with ethyl acetate, washed with water, and dried with Na_2SO_4. Ethyl acetate was removed, and the residue was crystallised from acetone–hexane.

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-dimethyl-3-azabicyclo[3.1.0]hex-2-ene 5b. Mp 170–172°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 1.27 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 3.24 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 7.30 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 15.31 q, 21.53 q, 39.22 s, 40.21 s, 40.52 s, 48.81 q, 51.32 q, 113.31 s, 114.72 s, 117.11 s, 157.33 s. Anal. calcd for $C_{11}H_{14}N_4O_2$: C, 56.41; H, 5.98; N, 23.93. Found: C, 56.65; H, 5.91; N, 24.12.

2-Amino-1,5-dicyano-4,4-diethoxy-6,6-dimethyl-3-azabicyclo[3.1.0]hex-2-ene 5c. Mp 130–132°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 1.05–1.15 (t, 6H, CH_3), 1.25 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 3.40–3.70 (m, 4H, OCH_2), 7.25 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 14.82 q, 15.21 q, 15.53 q, 21.51 q, 39.03 s, 40.11 s, 41.02 s, 56.91 t, 59.32 t, 113.41 s, 114.73 s, 116.42 s, 157.01 s. Anal. calcd for $C_{13}H_{18}N_4O_2$: C, 59.54; H, 6.87; N, 21.37. Found: C, 59.37; H, 6.98; N, 21.19.

2-Amino-1,5-dicyano-6-ethyl-4,4-dimethoxy-6-methyl-3-azabicyclo[3.1.0]hex-2-ene 5d (mixture of two isomers). Mp 153–155°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 0.97 and 1.13 (t, 6H, CH_3), 1.24 and 1.48 (s, 3H, CH_3), 1.75 (m, 4H, CH_2), 3.25 and 3.26 (s, 6H, OCH_3), 7.35 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 9.42 q, 10.11 q, 11.63 q, 16.32 q, 21.33 t, 28.51 t, 40.01 s, 40.13 s, 41.82 s, 43.41 s, 43.62 s, 48.81 q, 51.32 q, 113.21 s, 113.42 s, 114.41 s, 114.43 s, 116.91 s, 116.92 s, 157.03 s, 157.31 s. Anal. calcd for $C_{12}H_{16}N_4O_2$: C, 58.06; H, 6.45; N, 22.58. Found: C, 58.28; H, 6.54; N, 22.32.

2-Amino-1,5-dicyano-4,4-dimethoxy-6-propyl-3-azabicyclo[3.1.0]hex-2-ene 5e. Mp 187–189°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 0.95 (t, 3H, CH_3), 1.55 (m, 2H, CH_3), 1.74 (m, 2H, CH_2), 3.24 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 3.83 (t, 1H, CH), 7.32 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 14.11 q, 18.82 t, 19,13 t, 39.21 s, 41.13 s, 41.82 d, 49.31 q, 51.92 q, 112.71 s, 112.73 s, 117.72 s, 157.63 s. Anal. calcd for $C_{12}H_{16}N_4O_2$: C, 58.06; H, 6.45; N, 22.58. Found: C, 57.95; H, 6.37; N, 22.67.

2-Amino-1,5-dicyano-4,4-dimethoxy-6-methyl-6-propyl-3-azabicyclo[3.1.0]hex-2-ene 5f (mixture of two isomers). Mp 127–129°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 0.92 and 0.96 (t, 3H, CH_3), 1.21 and 1.49 (s, 3H, CH_3), 1.45–1.85 (m, 4H, CH_3), 3.24 and 3.25 (s, 6H, OCH_3), 7.29 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 12.31 q, 14.01 q, 14.22 q, 14.41 q, 18.62 t, 18.71 t, 19.03 t, 19.11 t, 30.12 s, 40.03 s, 40.11 s, 40.82 s, 42.21 s, 42.44 s, 42.61 s, 48.82 q, 49.31 q, 51.21 q, 51.53 q, 113.41 s, 113.43 s, 114.82 s, 114.84 s, 117.21 s, 117.23 s, 157.22 s, 157.23 s. Anal. calcd for $C_{13}H_{18}N_4O_2$: C, 59.54; H, 6.87; N, 21.37. Found: C, 59.31; H, 6.80; N, 21.45.

2-Amino-1,5-dicyano-4,4-diethoxy-6-phenyl-3-azabicyclo-[3.1.0]hex-2-ene 5g. Mp 247–249°C (decomp.), ^{1}H NMR

(DMSO-d_6): δ 1.07 and 1.11 (t, 6H, CH_3), 3.50 and 3.70 (m, 4H, CH_2O), 5.25 (s, 1H, CH), 7.29 (s, 2H, NH_2), 7.70–7.80 (m, 5H, C_6H_5). ^{13}C NMR (DMSO-d_6): δ 15.02 q, 15.21 q, 35.43 s, 38.21 s, 41.42 s, 57.73 t, 59.32 t, 112.31 s, 113.52 s, 118.14 s, 128.80 d, 128.83 d, 129.06 d, 129.73 s, 159.01 s. Anal. calcd for $C_{17}H_{18}N_4O_2$: C, 65.81; H, 5.81; N, 18.06. Found: C, 65.74; H, 5.75; N, 18.27.

2-Amino-1,5-dicyano-4,4-dimethoxy-6,6-tetramethylene-3-azabicyclo[3.1.0]hex-2-ene 5h. Mp 215–217°C (decomp.), ^{1}H NMR (DMSO-d_6): δ 1.40–2.10 (m, 8H, CH_2), 3.24 (s, 3H, CH_3O), 3.26 (s, 3H, CH_3O), 7.32 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6): δ 27.54 t, 27.56 t, 32.31 t, 32.34 t, 39.13 s, 40.21 s, 40.72 s, 48.93 q, 51.52 q, 113.71 s, 113.72 s, 117.30 s, 157.31 s. Anal. calcd for $C_{13}H_{16}N_4O_2$: C, 60.03; H, 6.15; N 21.54. Found: C, 60.15; H, 6.07; N 21.37.

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