

A new strategy of the chemical route to the cyclopropane structure: direct transformation of benzylidenemalononitriles and malononitrile into 1,1,2,2-tetracyanocyclopropanes

Michail N. Elinson*, Sergey K. Feducovich, Nikita O. Stepanov, Anatolii N. Vereshchagin, Gennady I. Nikishin

N.D. Zelinsky Institute of Organic Chemistry, Leninsky prospect 47, 119991 Moscow, Russia

Received 23 July 2007; received in revised form 24 October 2007; accepted 8 November 2007

Available online 12 November 2007

Abstract

The new reaction was found: the direct formation of cyclopropanes from activated olefins and C–H acids. The action of free halogen or active halogen containing compounds on the equal amounts of benzylidenemalononitriles and malononitrile in basic alcohol solutions results in the formation of 3-aryl-1,1,2,2-tetracyanocyclopropanes in 65–95% yields. Thus, the new simple and efficient way to 3-aryl substituted tetracyanocyclopropanes was found directly from such simple and reasonable starting compounds as benzylidenemalononitriles and malononitrile. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Malononitrile; Benzylidenemalononitriles; Tetracyanocyclopropanes; Cyclopropane formation

1. Introduction

Malononitrile is a commonly known and widely used reagent in the synthesis of heterocyclic compounds, pharmaceuticals, pesticides, fungicides, and solvatochromic dyes. The unique reactivity of this compound has led to its widespread application in organic chemistry, as well as or even more than other C–H acids such as malonate and cyanoacetic esters.¹

The use of alkylidenemalononitriles, which contain an activated double bond together with two reactive CN groups, is also quite common in organic synthesis. The ever-increasing interest in different addition, cyclization, and condensation reactions with alkylidenemalononitriles will undoubtedly continue.²

The cyclopropyl group is also a vital structural unit in many synthetic and naturally occurring compounds, exhibiting a wide spectrum of biologic properties ranging from enzyme inhibition to herbicidal, antibiotic, antitumor, and antiviral

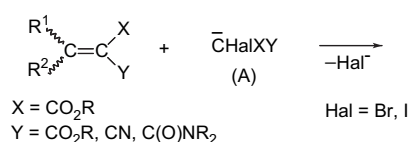
activities.^{3–5} Insecticidal pyrethrins (derivatives of cyclopropanoid chrysanthemic acid) are perhaps the best known example of their use.³ Thus, the prevalence of cyclopropane containing compounds with biological activity, whether isolated from natural sources or rationally designed pharmaceutical agents, has inspired chemists to find novel and diverse approaches to their synthesis.

Though the methods of cyclopropanes synthesis have long been documented, so far, all of them consist of two main groups: (1) intramolecular cyclization or (2) interaction of two different molecules (addition of carbenes to olefins or Michael initiated ring closure (MIRC) are the most known examples of this type).^{3,5} MIRC play an important role in organic chemistry and many synthetic applications are described in the literature so far.⁶

The well-known method of MIRC synthesis of substituted cyclopropanes involves addition of halogenosubstituted C–H acid anions (A), generated by the action of a base on the corresponding C–H acid (AH), to the conjugated activated olefins followed by cyclization with elimination of halogen anion⁷ (Scheme 1).

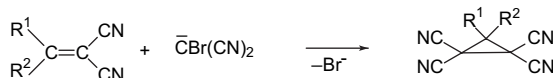
* Corresponding author. Tel.: +7 495 137 38 42; fax: +7 495 135 53 28.

E-mail address: elinson@ioc.ac.ru (M.N. Elinson).



Scheme 1.

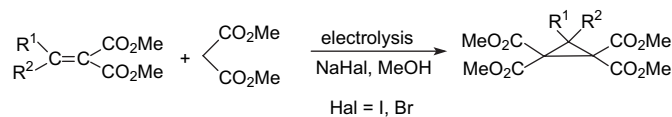
This method was used for the syntheses of tetracyanosubstituted cyclopropanes from alkylidene- or benzylidenemalononitriles and bromomalononitrile^{8–12} with one exception—the base was omitted because bromomalononitrile is a reasonably strong acid,¹³ which can furnish a sufficient concentration of bromodicyanocarbanion¹⁴ for the reaction. The yields of the tetracyanocyclopropanes were in the range of 30–90% (Scheme 2), but the excess (1.3–3.0 equiv) of bromomalononitrile was commonly used,^{8,9} and the usual reaction time took 10–20 h.^{8,9} Moreover, in some cases the reaction time was as long as 1–6 days.⁸



Scheme 2.

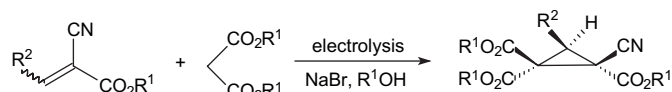
3-Phenyl-1,1,2,2-tetracyanocyclopropane was obtained in 95% yield through the reaction of 3-fold excess of benzylidenemalononitrile with dibromomalononitrile in the presence of equimolar quantity of rare indium powder and 0.2 equiv of lithium iodide as catalyst in dimethylformamide.¹⁵

The next essential step in the cyclopropane ring construction was connected with the electrochemical technique and using halogen containing mediatory systems in an undivided cell. Thus, the new electrochemical approach to functionally substituted cyclopropanes was performed by the electrolysis of alkylidenemalonates and malonate in an undivided cell in methanol in the presence of halides as mediators¹⁶ (Scheme 3).



Scheme 3.

The co-electrolysis of alkylidenecyanoacetic and malonic esters carried out within the guidelines of this approach resulted in the stereoselective synthesis of (*E*)-isomers of trialkyl 3-substituted-2-cyanocyclopropane-1,1,2-tricarboxylates¹⁷ (Scheme 4).



Scheme 4.

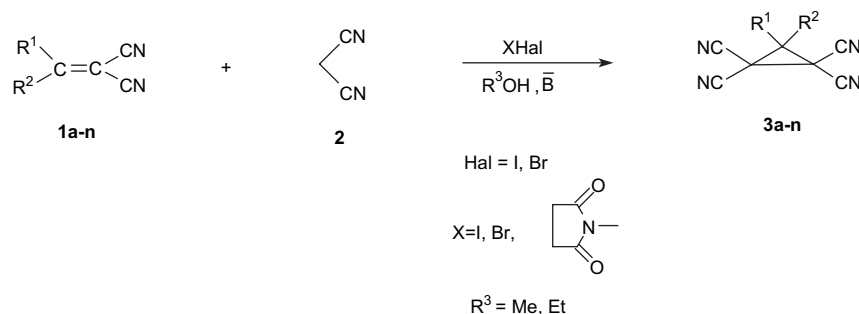
We have recently accomplished electrocatalytic transformation of alkylidenemalononitriles and malonates into dialkyl 3-substituted-2,2-dicyanocyclopropane-1,1-dicarboxylates¹⁸ and also alkylidenemalononitriles and malononitrile into 3-substituted 1,1,2,2-tetracyanocyclopropanes in 50–90% yields.¹⁹

Nevertheless, any new one-step and efficient chemical approach to substituted 1,1,2,2-tetracyanocyclopropanes starting from simple and reasonable compounds is welcome.

2. Results and discussion

This communication deals with new direct chemical transformation of alkylidenemalononitriles **1a–n** and malononitrile **2** into tetracyanosubstituted cyclopropanes **3a–n** realized under the action of active halogen containing compounds (Scheme 5).

First, to evaluate the synthetic potential of the procedure proposed and to optimize the conditions, the transformation of benzylidenemalononitrile **1a** and malononitrile **2** into 3-phenyl-1,1,2,2-tetracyanocyclopropane **3a** was studied (Table 1).



- a** $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$; **b** $\text{R}^1 = \text{H}, \text{R}^2 = 4\text{-MeC}_6\text{H}_4$; **c** $\text{R}^1 = \text{H}, \text{R}^2 = 2\text{-MeOC}_6\text{H}_4$; **d** $\text{R}^1 = \text{H}, \text{R}^2 = 3\text{-MeOC}_6\text{H}_4$;
e $\text{R}^1 = \text{H}, \text{R}^2 = 4\text{-MeOC}_6\text{H}_4$; **f** $\text{R}^1 = \text{H}, \text{R}^2 = 4\text{-FC}_6\text{H}_4$; **g** $\text{R}^1 = \text{H}, \text{R}^2 = 2\text{-ClC}_6\text{H}_4$; **h** $\text{R}^1 = \text{H}, \text{R}^2 = 3\text{-ClC}_6\text{H}_4$;
i $\text{R}^1 = \text{H}, \text{R}^2 = 4\text{-ClC}_6\text{H}_4$; **j** $\text{R}^1 = \text{H}, \text{R}^2 = 2\text{-Cl(4-Cl)C}_6\text{H}_3$; **k** $\text{R}^1 = \text{H}, \text{R}^2 = 3\text{-BrC}_6\text{H}_4$; **l** $\text{R}^1 = \text{H}, \text{R}^2 = 4\text{-NO}_2\text{C}_6\text{H}_4$;
m $\text{R}^1 = \text{H}, \text{R}^2 = n\text{-Pr}$; **n** $\text{R}^1 + \text{R}^2 = \text{-(CH}_2\text{)}_5\text{-}$

Scheme 5.

Table 1

Direct transformation of benzylidenemalononitrile **1a** and malononitrile **2** into 3-phenyl 1,1,2,2-tetracyanocyclopropane **3a** by the action of halogen or NBS in basic alcohols^a

No.	XHal	Base	R ³ OH	Yield of 3a ^b (%)
1	I ₂	KOH	MeOH	25
2	I ₂	KOH	EtOH	36
3	I ₂	EtONa	EtOH	51
4	NBS	NaOH	EtOH	35
5	NBS	KOH	EtOH	48
6	NBS	EtONa	EtOH	63
7	Br ₂	KOH	MeOH	44
8	Br ₂	KOH	EtOH	67
9	Br ₂	EtONa	EtOH	93
10 ^c	Br ₂	EtONa	EtOH	95

^a Reagents and conditions: 10 mmol of benzylidenemalononitrile, 10 mmol of malononitrile, 20 mL of alcohol, 12 mmol of base, 10 mmol of halogen or NBS, time of the reaction—3 h.

^b Isolated yields.

^c Malononitrile of 13 mmol.

The second step was devoted to careful evaluation of EtONa quantity needed for reaction (Table 2).

Table 2

Influence of EtONa quantity on 3-phenyl 1,1,2,2-tetra-cyanocyclopropane **3a** yield^a

No.	Quantity of EtONa (equiv)	Yield of 3a ^b (%)
1	0.5	63
2	1.0	78
3	1.2	93
4	1.5	65
5	2.0	34

^a Reagents and conditions: 10 mmol of benzylidenemalononitrile, 10 mmol of malononitrile, 20 mL of EtOH, 5–20 mmol of EtONa, 10 mmol of bromine, time of the reaction—3 h.

^b Isolated yields.

Excellent conversions of starting compounds and 93% yield of cyclopropane **3a** were obtained when the reaction was carried out in ethanol by the action of bromine in the presence of 1.2 equiv of EtONa (entry 9, Table 1 and entry 3, Table 2). The increase of malononitrile quantity had a little effect on the **3a** yield (entry 10, Table 1). The increase of EtONa quantity compared to 1.2 equiv (entries 4 and 5, Table 2) resulted in a sufficient decrease of the reaction yield, that may be connected with the activation of undesired base induced oligomerization processes of starting malononitrile¹ and benzylidenemalononitrile.^{2d,e}

Under the optimal conditions found i.e., bromine as active halogen compound, 1.2 equiv of EtONa as base, and ethanol as solvent, substituted benzylidenemalononitriles or alkylidenemalononitriles **1b–n** and malononitrile were transformed into corresponding substituted 1,1,2,2-tetracyanocyclopropanes **3b–n** in 65–92% yields (Table 3).

In the case of benzylidenemalononitriles **1e** and **1j** (entries 4 and 9, Table 3) the quantity of EtOH was increased up to 30 mL because of the lower solubility of **1e** and **1j** in EtOH. Thus, under conditions used, 3-substituted 1,1,2,2-tetracyanocyclopropanes **3a–n** were obtained in 65–95% yields, among them 3-propyl substituted cyclopropane **3m** and

Table 3

Direct transformation of substituted benzylidenemalononitriles **1b–n** and malononitrile **2** into substituted 1,1,2,2-tetracyanocyclopropanes **3b–n** by the action of bromine in EtOH/EtONa system^a

No.	R ¹	R ²	Benzylidene-malononitrile	Product, yield ^b (%)
1	H	4-MeC ₆ H ₄	1b	3b , 84
2	H	2-MeOC ₆ H ₄	1c	3c , 89
3	H	3-MeOC ₆ H ₄	1d	3d , 92
4	H	4-MeOC ₆ H ₄ ^c	1e	3e , 75
5	H	4-FC ₆ H ₄	1f	3f , 81
6	H	2-ClC ₆ H ₄	1g	3g , 79
7	H	3-ClC ₆ H ₄	1h	3h , 72
8	H	4-ClC ₆ H ₄	1i	3i , 87
9	H	2-Cl(4-Cl)C ₆ H ₃ ^c	1j	3j , 65
10	H	3-BrC ₆ H ₄	1k	3k , 68
11	H	4-NO ₂ C ₆ H ₄	1l	3l , 71
12	H	<i>n</i> -Pr	1m	3m , 84
13		-(CH ₂) ₅ -	1n	3n , 75

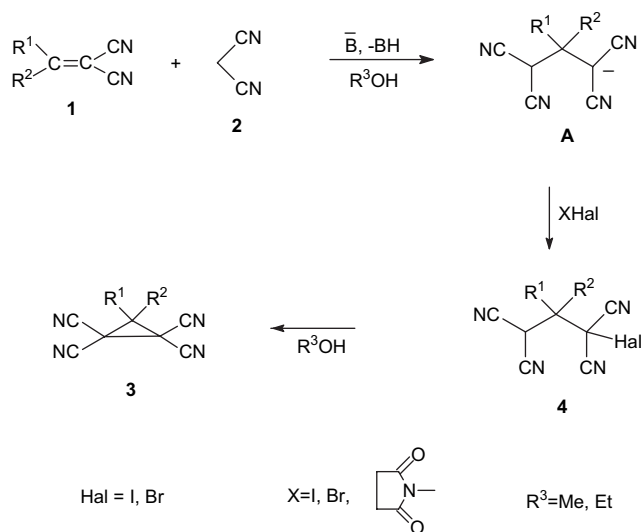
^a Reagents and conditions: 10 mmol of benzylidenemalononitrile, 10 mmol of malononitrile, 20 mL of EtOH, 12 mmol of EtONa, 10 mmol of bromine, time of the reaction—3 h.

^b Isolated yields.

^c EtOH: 30 mL.

spirocyclopropane **3n**. Hence the method is useful for the synthesis of tetracyanocyclopropanes from alkylidenemalononitriles and malononitrile as well as from cycloalkylidenemalononitriles and malononitrile (entries 12 and 13, Table 3).

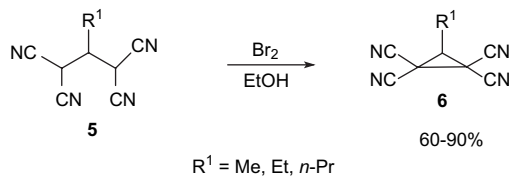
Taking into consideration the data obtained, the following reaction scheme for the transformation of benzylidene- or alkylidenemalononitriles **1a–n** and malononitrile **2** into substituted tetracyanocyclopropanes **3a–n** is proposed (Scheme 6).



Scheme 6.

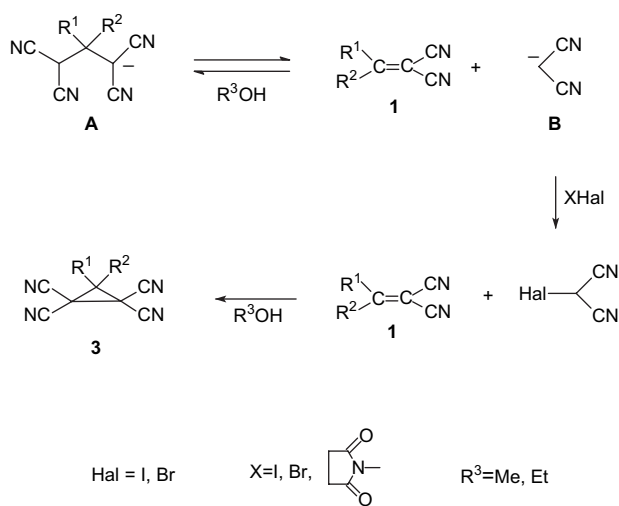
The Michael addition of malononitrile to benzylidene- or alkylidenemalononitrile **1** in the presence of the base results in the anion **A** formation. Earlier formation of anion **A** from benzylidenemalononitrile and malononitrile was observed under basic conditions.²⁰

Then halogenation of anion **A** by the action of active halogen containing compound leads to substituted 1-halogeno-1,1,3,3-tetracyanopropane **4**. The following cyclization of **4** into tetracyanocyclopropane **3** in alcoholic solutions takes place in accordance with the earlier reported data.¹⁴ It should be especially mentioned that the last step of the mechanism (Scheme 6) is a part of the tetracyanocyclopropane synthesis suggested by Mariella and Roth.¹⁴ This method includes bromination of 2-alkyl substituted 1,1,3,3-tetracyanopropanes **5** with instant formation of 3-alkyl substituted 1,1,2,2-tetracyanocyclopropanes **6** in 60–90% yields (Scheme 7).¹⁴



Scheme 7.

Taking into consideration that anion **A** exists in alcoholic solutions in equilibrium with benzylidene- or alkylidenemalononitrile **1** and anion of malononitrile **B**²⁰ the following alternative mechanism of tetracyanocyclopropanes **3** formation could also take place (Scheme 8).



Scheme 8.

The last step of the Scheme 8 mechanism corresponds to tetracyanocyclopropane synthesis reported by Hart and Kim (Scheme 2),^{8,9} which includes addition of the 1.3–3.0 equiv excess of bromomalononitrile to alkylidene-, benzylidene- and α -arylalkylidenemalononitriles in 50–95% aqueous ethanol with formation of substituted 1,1,2,2-tetracyanocyclopropanes in 30–90% yields.

3. Conclusions

Thus, the new reaction was found, namely the direct formation of cyclopropane structures from activated olefins and

C–H acids. The action of free halogen or active halogen containing compounds on the equal amounts of benzylidene- or alkylidenemalononitriles and malononitrile in basic alcohol solutions results in the formation of 3-substituted 1,1,2,2-tetracyanocyclopropanes in 65–95% yields. The latter are well-known precursors for different bicyclic heterosystems, among them containing cyclopropane ring^{19a,21} and possessing different types of pharmacological activity.^{3,22} The new simple and efficient way to 3-aryl substituted tetracyanocyclopropanes was found starting from such simple and reasonable compounds as benzylidenemalononitriles and malononitrile. The procedure utilizes inexpensive reagents, it is easily carried out and the work up is not complicated. 3-Aryl substituted-1,1,2,2-tetracyanocyclopropanes are crystallized directly from the reaction mixture, consequently, the isolation includes only filtration and washing with warm water.

Compared to the MIRC method suggested by Hart and Kim⁸ this new one uses equimolar amount of malononitrile instead of the excess of bromomalononitrile. Thus, the stage of bromomalononitrile synthesis is omitted. As compared with the method of bromination and further intramolecular cyclization of 2-substituted 1,1,3,3-tetracyanopropanes reported by Mariella and Roth,¹⁴ it should be mentioned that this method is known only for a few examples (only for three 2-alkyl substituted 1,1,3,3-tetracyanopropanes; alkyl=methyl, ethyl and *n*-propyl), which is connected with complexity of the synthesis and isolation of 2-substituted 1,1,3,3-tetracyanopropanes.

4. Experimental section

4.1. General remarks

All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded with Bruker AC-200, Bruker WM-250, and Bruker AC-300 spectrometers at ambient temperature. Chemical shifts values are relative to Me₄Si. IR spectra were registered with a SPECORD M82 spectrometer in KBr pellets. Mass-spectra (EI=70 eV) were obtained directly with a Finningan MAT INCOS 50 spectrometer.

4.2. Typical procedure

To a 10 mL ethanol solution of benzylidenemalononitrile **1** (10 mmol) and malononitrile **2** (10 mmol) in a 50 mL beaker, 12 mmol of base in 10 mL of ethanol was added for 1 min. Then 10 mmol of halogen or *N*-bromosuccinimide was added without cooling. The mixture was magnetically stirred at room temperature for 3 h. Then solid phase was filtered off, washed with warm water, and dried in desiccator over P₂O₅ to isolate pure **3a–n**.

All compounds (**3a–n**) gave expected NMR spectra. For new compounds (**3f,k**), satisfactory elemental analyses, mass, and IR spectroscopy data were obtained.

4.2.1. 3-Phenyl-1,1,2,2-tetracyanocyclopropane (**3a**)

White solid. Yield 2.07 g (95%); m p 229–230 °C (acetone–hexane); lit. mp⁹ 227–230 °C; δ_{H} (250 MHz, DMSO-*d*₆) 5.10 (1H, s, CH), 7.48–7.80 (5H, m, Ar).

4.2.2. 3-(4-Methylphenyl)-1,1,2,2-tetracyanocyclopropane (**3b**)

White solid. Yield 1.95 g (84%); mp 226–227 °C (acetone–hexane); lit. mp⁹ 227–230 °C; δ_{H} (250 MHz, DMSO-*d*₆) 2.31 (3H, s, CH₃), 5.20 (1H, s, CH), 7.28 (2H, d, *J* 8.0 Hz, Ar), 7.65 (2H, d, *J* 8.0 Hz, Ar).

4.2.3. 3-(2-Methoxyphenyl)-1,1,2,2-tetracyanocyclopropane (**3c**)²³

White solid. Yield 2.21 g (89%); mp 240–241 °C (acetone–hexane); δ_{H} (250 MHz, DMSO-*d*₆) 3.89 (3H, s, OCH₃), 5.04 (1H, s, CH), 7.05 (1H, t, *J* 7.5 Hz, Ar), 7.19 (1H, d, *J* 8.3 Hz, Ar), 7.48 (1H, t, *J* 7.9 Hz, Ar), 7.76 (1H, d, *J* 7.5 Hz, Ar); δ_{C} (75 MHz, DMSO-*d*₆) 23.6, 38.9, 56.5, 110.1, 111.4, 112.1, 115.2, 121.1, 130.5, 132.2, 157.9; MS (70 eV) *m/z* (relative intensity %): 248 ([M⁺], 100), 233 (58), 221 (57), 206 (36), 194 (17), 178 (26), 156 (28), 114 (57), 91 (67), 77 (43); IR (KBr): ν_{max} 2262, 1604, 1436, 1253, 764 cm^{−1}; C₁₄H₈N₄O: calcd (%) C 67.74, H 3.25, N 22.57, found (%): C 67.62, H 3.12, N 22.38.

4.2.4. 3-(3-Methoxyphenyl)-1,1,2,2-tetracyanocyclopropane (**3d**)

White solid. Yield 2.28 g (92%); mp 227–229 °C (acetone–hexane); lit. mp^{19a} 227–230 °C; δ_{H} (200 MHz, DMSO-*d*₆) 3.76 (3H, s, OCH₃), 5.28 (1H, s, CH), 7.15–7.45 (4H, m, Ar).

4.2.5. 3-(4-Methoxyphenyl)-1,1,2,2-tetracyanocyclopropane (**3e**)

White solid. Yield 1.86 g (75%); mp 208–210 °C (acetone–hexane); lit. mp²² 209–210 °C; δ_{H} (250 MHz, DMSO-*d*₆) 3.77 (3H, s, OCH₃), 5.12 (1H, s, CH), 7.02 (2H, d, *J* 8.9 Hz, Ar), 7.71 (2H, d, *J* 8.9 Hz, Ar).

4.2.6. 3-(4-Fluorophenyl)-1,1,2,2-tetracyanocyclopropane (**3f**)

White solid. Yield 1.91 g (81%); mp 216–217 °C (acetone–hexane); δ_{H} (250 MHz, DMSO-*d*₆) 5.23 (1H, s, CH), 7.34 (2H, t, *J* 8.5 Hz, Ar), 7.89 (2H, dd, *J*₁ 8.5, *J*₂ 5.4 Hz, Ar); δ_{C} (75 MHz, DMSO-*d*₆) 23.8, 41.5, 109.9, 111.4, 116.5 (d, ²*J*_{CF} 21.8 Hz), 123.7 (d, ⁴*J*_{CF} 3.0 Hz), 132.6 (d, ³*J*_{CF} 8.6 Hz), 163.3 (d, ¹*J*_{CF} 246.3 Hz); δ_{F} (282 MHz, DMSO-*d*₆) −111.5 to −111.6 (m); MS (70 eV) *m/z* (relative intensity %): 236 ([M⁺], 24), 209 (66), 182 (16), 172 (34), 159 (19), 145 (46), 121 (49), 108 (100); IR (KBr): ν_{max} 2264, 1604, 1512, 1220, 848 cm^{−1}; C₁₃H₅FN₄: calcd (%) C 66.10, H 2.13, F 8.04, N 23.72, found (%): C 65.89, H 2.28, F 7.86, N 23.41.

4.2.7. 3-(2-Chlorophenyl)-1,1,2,2-tetracyanocyclopropane (**3g**)

White solid. Yield 1.99 g (79%); mp 245–247 °C (acetone–hexane); lit. mp⁹ 246–248 °C; δ_{H} (250 MHz, DMSO-*d*₆) 5.47 (1H, s, CH), 7.50–7.65 (2H, m, Ar), 7.72 (1H, d, *J* 7.8 Hz, Ar), 8.06 (1H, d, *J* 7.5 Hz, Ar).

4.2.8. 3-(3-Chlorophenyl)-1,1,2,2-tetracyanocyclopropane (**3h**)

White solid. Yield 1.82 g (72%); mp 187–189 °C (acetone–hexane); lit. mp⁹ 183–185 °C; δ_{H} (250 MHz, DMSO-*d*₆) 5.37 (1H, s, CH), 7.50–7.60 (2H, m, Ar), 7.82 (1H, d, *J* 3.7 Hz, Ar), 8.09 (1H, s, Ar).

4.2.9. 3-(4-Chlorophenyl)-1,1,2,2-tetracyanocyclopropane (**3i**)

White solid. Yield 2.20 g (87%); mp 250–251 °C (acetone–hexane); lit. mp⁹ 248–250 °C; δ_{H} (300 MHz, DMSO-*d*₆) 5.28 (1H, s, CH), 7.59 (2H, d, *J* 8.5 Hz, Ar), 7.88 (2H, d, *J* 8.5 Hz, Ar).

4.2.10. 3-(2,4-Dichlorophenyl)-1,1,2,2-tetracyanocyclopropane (**3j**)

White solid. Yield 1.87 g (65%); mp 226–228 °C (acetone–hexane); lit. mp⁹ 225–228 °C; δ_{H} (300 MHz, DMSO-*d*₆) 5.48 (1H, s, CH), 7.66 (1H, dd, *J*₁ 8.5, *J*₂ 2.0 Hz, Ar), 7.93 (1H, d, *J* 2.0 Hz, Ar), 8.10 (1H, d, *J* 8.5 Hz, Ar).

4.2.11. 3-(3-Bromophenyl)-1,1,2,2-tetracyanocyclopropane (**3k**)

White solid. Yield 2.02 g (68%); mp 186–187 °C (acetone–hexane); δ_{H} (250 MHz, DMSO-*d*₆) 5.31 (1H, s, CH), 7.44 (1H, t, *J* 8.5 Hz, Ar), 7.68 (1H, d, *J* 8.5 Hz, Ar), 7.87 (1H, d, *J* 8.5 Hz, Ar), 8.22 (1H, s, Ar); δ_{C} (75 MHz, DMSO-*d*₆) 23.4, 40.6, 109.5, 110.9, 121.9, 128.8, 129.5, 131.1, 132.6, 132.9; MS (70 eV) *m/z* (relative intensity %): 298 (M⁺, 12), 296 (M⁺, 11), 234 (6), 232 (6), 217 (99), 190 (100), 153 (56), 126 (87), 100 (39), 89 (60); IR (KBr): ν_{max} 2268, 1568, 1484, 780, 692 cm^{−1}; C₁₃H₅BrN₄: calcd (%) C 52.55, H 1.70, Br 26.89, N 18.86, found (%): C 52.39, H 1.86, Br 26.72, N 18.70.

4.2.12. 3-(4-Nitrophenyl)-1,1,2,2-tetracyanocyclopropane (**3l**)

White solid. Yield 1.87 g (71%); mp 232–234 °C (acetone–hexane); lit. mp⁹ 232–235 °C; δ_{H} (250 MHz, DMSO-*d*₆) 5.52 (1H, s, CH), 8.20 (2H, d, *J* 8.8 Hz, Ar), 8.35 (2H, d, *J* 8.8 Hz, Ar).

4.2.13. 3-Propyl-1,1,2,2-tetracyanocyclopropane (**3m**)

White solid. Yield 1.55 g (84%); mp 136–138 °C (acetone–hexane); lit. mp^{19a} 136–138 °C; δ_{H} (200 MHz, CDCl₃) 1.13 (3H, t, *J* 7.3 Hz, CH₃), 1.60–1.85 (2H, m, CH₂), 1.94 (2H, q, *J* 7.3 Hz, CH₂) 2.78 (1H, t, *J* 7.3 Hz, CH).

4.2.14. 1,1,2,2-Tetracyanospiro[2.5]octane (**3n**)

White solid. Yield 1.58 g (75%); mp 178–180 °C (acetone–hexane); lit. mp⁸ 177–179 °C; δ_{H} (200 MHz, DMSO-*d*₆)

1.45–1.55 (2H, m, CH₂), 1.60–1.75 (4H, m, 2CH₂), 1.80–1.95 (4H, m, 2CH₂).

Acknowledgements

The authors gratefully acknowledge the financial support of the Presidential Scholarship Program for State Support of Leading Science Schools of Russian Federation (Project No. 5022.2006.3).

References and notes

- For selected reviews, see: (a) Freeman, F. *Chem. Rev.* **1969**, *69*, 591–624; (b) Fatiadi, A. J. *Synthesis* **1978**, 165–204; (c) Fatiadi, A. J. *Synthesis* **1978**, 241–282; (d) Saikia, A. *Synlett* **2004**, 2247–2248.
- (a) Mokrosz, M. J. *Arch. Pharm.* **1993**, *326*, 39–43; (b) Lohmeyer, B.; Margaretha, P. *Photochem. Photobiol. Sci.* **2005**, *4*, 637–640; (c) Krasnaya, Z. A.; Tret'yakova, E. O.; Zlotin, S. G. *Mendeleev Commun.* **2006**, 326–327; For reviews see: (d) Campaigne, F.; Sohneller, S. W. *Synthesis* **1976**, 705–716; (e) Freeman, F. *Chem. Rev.* **1980**, *80*, 329–350.
- (a) Yanovskaya, L. A.; Dombrovsky, V. A.; Khusid, A. Kh. *Tsiklopropani s funktsionalnimi gruppami. Sintez i primeneniye. (Cyclopropanes with Functional Groups. Synthesis and Application)*; Nauka: Moscow, 1980; (b) Tsuji, T.; Nishida, S. *The Chemistry of the Cyclopropyl Group*; Wiley and Sons: New York, NY, 1987; (c) Boche, G.; Walbirsky, H. M. *Cyclopropane Derived Intermediates*; John Wiley and Sons: New York, NY, 1990; (d) Rappoport, Z. *The Chemistry of the Cyclopropyl Group*; Wiley and Sons: New York, NY, 1996.
- (a) Baba, Y.; Saha, G.; Nakao, S.; Iwata, C.; Tanaka, T.; Ibuka, T.; Ohishi, H.; Takemoto, Y. *J. Org. Chem.* **2001**, *66*, 81–88; (b) Boger, D. L.; Hughes, T. V.; Hedrick, M. P. *J. Org. Chem.* **2001**, *66*, 2207–2216; (c) Graham, D. W.; Ashton, W. T.; Barash, L.; Brown, J. E.; Brown, R. D.; Canning, L. F.; Chen, A.; Springer, J. P.; Rogers, E. F. *J. Med. Chem.* **1987**, *30*, 1074–1090; (d) Yoshida, S.; Rosen, T. C.; Meyer, O. G. J.; Sloan, M. J.; Ye, S.; Haufe, G.; Kirk, K. L. *Bioorg. Med. Chem.* **2004**, *12*, 2645–2652.
- For reviews see: (a) Faust, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2251–2253; (b) Donaldson, W. A. *Tetrahedron* **2001**, *57*, 8589–8627; (c) Brandt, W.; Thiemann, T. *Chem. Rev.* **2003**, *103*, 1625–1647.
- (a) Little, R. D.; Dawson, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 4607–4609; (b) Little, R. D.; Dawson, J. R. *Tetrahedron Lett.* **1980**, *21*, 2609–2612; For reviews see: (c) Caine, D. *Tetrahedron* **2001**, *57*, 2643–2684; (d) Lebel, H.; Marcoux, J. F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 1016–1036.
- (a) Widman, O. *Ber.* **1918**, *51*, 533–541; (b) Westoo, G. *Acta Chem. Scand.* **1959**, *13*, 683–688; (c) Warner, D. T. *J. Org. Chem.* **1959**, *24*, 1536–1539; (d) Bonavent, G.; Causse, M.; Guitard, M.; Fraisse-Julien, R. *Bull. Soc. Chim. Fr.* **1964**, 2462–2471; (e) McCoy, L. L. *J. Org. Chem.* **1964**, *29*, 240–241.
- Hart, H.; Kim, Y. C. *J. Org. Chem.* **1966**, *31*, 2784–2789.
- Kim, Y. C.; Hart, H. *Tetrahedron* **1969**, *25*, 3869–3877.
- Horf, H.; Kreutzer, M. *Angew. Chem.* **1990**, *102*, 425–426.
- Nasakin, O. E.; Lukin, P. M.; Sadovoi, V. A. *Zh. Org. Khim.* **1993**, *29*, 1917.
- Kayukova, O. V.; Kayukov, Ya. S.; Lapteva, E. S.; Bardasov, I. N.; Ershov, O. V.; Nasakin, O. E. *Zh. Org. Khim.* **2006**, *42*, 1427–1429.
- Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439–2443.
- Mariella, R. P.; Roth, A. J. *J. Org. Chem.* **1957**, *22*, 1130–1133.
- Araki, S.; Butsugan, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1286–1287.
- Elinson, M. N.; Feducovich, S. K.; Zakharenkov, A. A.; Bushuev, S. G.; Pashchenko, D. V.; Nikishin, G. I. *Mendeleev Commun.* **1998**, 15–17.
- (a) Elinson, M. N.; Feducovich, S. K.; Starikova, Z. A.; Olessova, O. S.; Vereshchagin, A. N.; Nikishin, G. I. *Tetrahedron Lett.* **2000**, *41*, 4937–4941; (b) Elinson, M. N.; Feducovich, S. K.; Starikova, Z. A.; Vereshchagin, A. N.; Belyakov, P. A.; Nikishin, G. I. *Tetrahedron* **2006**, *62*, 3989–3996.
- Elinson, M. N.; Feducovich, S. K.; Zaimovskaya, T. A.; Vereshchagin, A. N.; Gorbunov, S. G.; Nikishin, G. I. *Izv. Akad. Nauk Ser. Khim.* **2005**, 1547–1552.
- (a) Elinson, M. N.; Feducovich, S. K.; Lizunova, T. L.; Nikishin, G. I. *Tetrahedron* **2000**, *56*, 3063–3070; (b) Elinson, M. N.; Feducovich, S. K.; Vereshchagin, A. N.; Dorofeev, A. S.; Dmitriev, D. E.; Nikishin, G. I. *Izv. Akad. Nauk Ser. Khim.* **2003**, 2117–2121.
- Bernasconi, C. F.; Zitomer, J. L.; Fox, J. P.; Howard, K. A. *J. Org. Chem.* **1984**, *49*, 482–486.
- (a) Takahashi, M.; Orihara, T.; Toshiaki, S.; Takanori, Y.; Yamatera, T.; Yamazaki, K.; Yoshida, A. *Heterocycles* **1986**, *24*, 2857–2862; (b) Nasakin, O. E.; Lukin, P. M.; Vershinin, E. V.; Yashkanova, O. V.; Lyshikov, A. N.; Urman, Ya. G.; Lindeman, S. V.; Struchkov, Yu. T.; Bulak, A. K. *Zh. Org. Khim.* **1995**, *31*, 370–374; (c) Lukin, P. M.; Manzenkov, A. V.; Urman, Ya. V.; Khrustalev, V. N.; Nesterov, V. N.; Antipin, M. Yu. *Zh. Org. Khim.* **2000**, *36*, 249–255; (d) Elinson, M. N.; Feducovich, S. K.; Zaimovskaya, T. A.; Vereshchagin, A. N.; Nikishin, G. I. *Izv. Akad. Nauk Ser. Khim.* **2003**, 2122–2127; (e) Kayukova, O. V.; Kayukov, Ya. S.; Nikolaev, A. N.; Ershov, O. V.; Eremkin, A. V.; Nasakin, O. E. *Zh. Org. Khim.* **2006**, *42*, 607–611.
- (a) Salaun, J.; Baird, M. S. *Curr. Med. Chem.* **1995**, *2*, 511–542; (b) Nasakin, O. E.; Lyshchikov, A. N.; Kayukov, Ya. S.; Sheverdov, V. P. *Khim.-Farm. Zh.* **2000**, *34*, 11–23.
- Usha, R.; Venkatesan, R. K. *Acta Crystallogr., Sect. B* **1980**, *36*, 335–339.