ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 7, pp. 1002–1007. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.V. Shchepin, Yu.G. Stepanyan, P.S. Silaichev, M.A. Ezhikova, M.I. Kodess, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 7, pp. 1009–1013.

Cyclopropanation of 2-Arylmethylidenemalononitriles, Alkyl 3-Aryl-2-cyanoprop-2-enoates, and N-Substituted 3-Aryl-2-cyanoprop-2-enamides with Bromine-Containing Zinc Enolates

V. V. Shchepin[†a], Yu. G. Stepanyan[a], P. S. Silaichev[a], M. A. Ezhikova[b], and M. I. Kodess[b]

[a] *Perm State University, ul. Bukireva 15, Perm, 614990 Russia*

[b] *Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia*

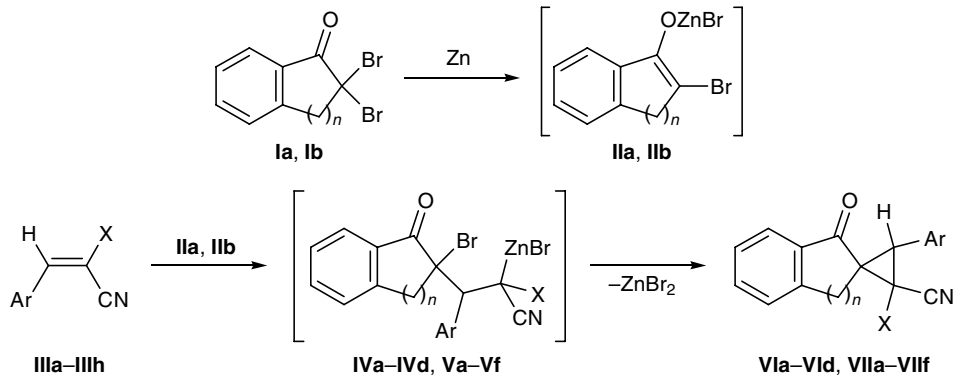
Received September 10, 2006

Abstract—Zinc enolates derived from 2,2-dibromoindan-1-one and 2,2-dibromo-1,2,3,4-tetrahydronaphthalen-1-one reacted with 2-arylmethylidenemalononitriles, alkyl 3-aryl-2-cyanoprop-2-enoates, and N-substituted 3-aryl-2-cyanoprop-2-enamides to give, respectively, 3-aryl-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitriles, 3-aryl-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitriles, alkyl 3-aryl-2-cyano-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2-carboxylates, alkyl 3-aryl-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxylates, and N-substituted 3-aryl-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxamides as a single diastereoisomer. The stereoconfiguration of the products was determined by ^{1}H and ^{13}C NMR spectroscopy.

DOI: 10.1134/S1070428007070111

Zinc enolates obtained from α,α-dibromo ketones are known to react with alkyl 3-aryl-2-cyanoprop-2-enoates and 3-aryl-2-cyanoprop-2-enamides to give polyfunctional cyclopropane derivatives [1, 2]. The present work was aimed at synthesizing cyclopropanation products having a spiro carbon atom via reactions of 2-arylmethylidenemalononitriles and alkyl 3-aryl-2-cyanoprop-2-enoates **IIIa**–**IIIh** with bromine-containing zinc enolates derived from 2,2-dibromoindan-1-one (**Ia**) and 2,2-dibromo-1,2,3,4-tetrahydronaphthalen-1-one (**Ib**). Zinc enolates **IIa** and **IIb** added at the double bond of electrophilic substrates **IIIa**–**IIIh** with

Scheme 1.



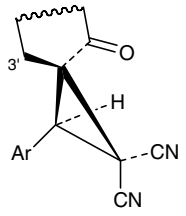
Ia, **IIa**, **IV**, **VI**, n = 1; **Ib**, **IIb**, **V**, **VII**, n = 2; **III**, X = CN, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 3-BrC_6H_4 (**c**), 3,4-$(MeO)_2C_6H_4$ (**d**); X = COOMe, Ar = 3-BrC_6H_4 (**e**), 4-BrC_6H_4 (**f**), 2,4-$Cl_2C_6H_3$ (**g**); X = COOEt, Ar = 2,4-$Cl_2C_6H_3$ (**h**); **IV**, **V**, X = CN, Ar = 4-ClC_6H_4 (**a**); X = COOMe, Ar = 4-BrC_6H_4 (**b**), 2,4-$Cl_2C_6H_3$ (**c**); X = COOEt, Ar = 2,4-$Cl_2C_6H_3$ (**d**); **VI**, **VII**, X = CN, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 3-BrC_6H_4 (**c**), 3,4-$(MeO)_2C_6H_4$ (**d**); X = COOMe, 4-BrC_6H_4 (**e**), 2,4-$Cl_2C_6H_3$ (**f**).

† Deceased.

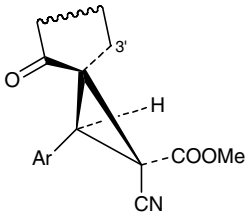
formation of intermediates **IVa–IVd** and **VIa–VIf** which underwent intramolecular cyclization to give the final products, 3-aryl-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitriles, alkyl 3-aryl-2-cyano-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2-carboxylates, 3-aryl-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitriles, and alkyl 3-aryl-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxylates **Va–Vd** and **VIIa–VIIf** (Scheme 1).

The structure of compounds **Va–Vd** and **VIIa–VIIf** was proved by elemental analysis and IR and NMR spectroscopy. Their IR spectra contained absorption bands due to stretching vibrations of the ketone carbonyl (1680–1710 cm^{-1}), ester carbonyl (1725–1745 cm^{-1}), and cyano groups (2210–2230 cm^{-1}). In order to determine stereoconfiguration of the products, we examined the ^1H and ^{13}C NMR spectra, including those obtained by two-dimensional homo- and heteronuclear NMR techniques (^1H–^1H COSY, ^1H–^1H NOESY, ^1H–^{13}C HSQC, and ^1H–^{13}C HMBC) of compounds **Va–Vc**, **VIIb**, **VIIe**, and **VIIf**. In the ^1H NMR spectra of these compounds we observed characteristic signals in the region δ 3.42–4.24 ppm from the CH proton in the three-membered ring. Signals in the ^1H and ^{13}C NMR spectra were assigned on the basis of the results of homo- and heteronuclear 2D experiments. The aromatic 4′-H proton in structures **Va–Vc** (5′-H in **VIIb**, **VIIe**, and **VIIf**) was identified by the presence of a cross peak in the 2D NOESY spectrum due to coupling with the CH_2 protons in the *peri* position (3′-H and 4′-H, respectively). In addition, these protons gave a cross peak in the 2D COSY-LR spectrum (recorded under conditions optimized for long-range couplings, $J_{HH} \leq 3$ Hz) due to long-range *ortho*-benzylic coupling. Analogous interactions were observed between 3-H and *ortho*-proton (6″-H) in compounds **Vc** and **VIIf** having a 2,4-dichlorophenyl substituent on C^3. The other aromatic protons in the indan or tetrahydronaphthalene fragments were successively assigned on the basis of the 2D ^1H–^1H COSY spectrum. Carbon atoms attached to protons were identified by cross peaks with the corresponding protons in the 2D HSQC spectra, while signals from quaternary carbon atoms were assigned on the basis of $^2J_{CH}$ and $^3J_{CH}$ coupling constants observed in 2D HMBC experiments.

The presence of only one set of signals in the ^1H and ^{13}C NMR spectra indicated that compounds **Va–Vc**, **VIIb**, **VIIe**, and **VIIf** were isolated as a single diastereoisomer. Steric configuration of their molecules is determined, on the one hand, by mutual orientation of the two spiro-fused rings and, on the other, by orientation of substituents at asymmetric carbon atoms in the cyclopropane ring. Stereochemical assignments were made by analysis of the coupling constants $^3J_{CH}$ between the 3-H proton in the three-membered ring and carbon atoms in the substituents, as well as by two-dimensional NOESY experiments.



Va, **VIIb**



Va, **Vc**, **VIIe**, **VIIf**

The coupling constants $^3J_{CH}$ between 3-H and carbon atom in the substituent on C^2 were measured from the ^{13}C NMR spectra recorded without decoupling from protons (see table). Taking into account the lack of published data on coupling constants between protons and cyano carbon atoms in cyclopropane derivatives **Va** and **VIIb** having similar substituents on C^2, these compounds seem to be convenient models for the determination of the corresponding *cis*- and *trans*-couplings. In keeping with the Karplus equation for cyclopropane derivatives, $J_{cis} > J_{trans}$; therefore, J_{cis} = 6.1 Hz, and J_{trans} = 4.5 Hz. For compounds **Vb**, **Vc**, **VIIe**, and **VIIf** in which the C^2 atom is asymmetric, the coupling constants ^3J(CN,3-H) range from 4.1 to 4.4 Hz; such values correspond to *trans* arrangement of the cyano group and 3-H and hence *cis* orientation of the ester group with respect to 3-H.

We failed to determine the coupling constants $^3J_{CH}$ between 3-H, on the one hand, and $C^{1'}$ and $C^{3'}$, on the other, with an acceptable accuracy; the corresponding carbon signals appeared in the proton-coupled spectra as complex unresolved multiplets. Information on

Coupling constants $^3J_{CH}$ for compounds **Va–Vc**, **VIIb**, **VIIe**, and **VIIf**

Compound no.	J_{cis}, Hz	J_{trans}, Hz
Va	6.1 (CN)	4.5 (CN)
Vb	4.6 (COO)	4.1 (CN)
Vc	4.3 (COO)	4.4 (CN)
VIIb	6.1 (CN)	4.5 (CN)
VIIe	5.1 (COO)	4.4 (CN)
VIIf	4.9 (COO)	4.4 (CN)

mutual orientation of the spiro-fused rings was obtained by analysis of the 2D NOESY spectra. Compounds **Vb**, **VIIe**, and **VIIf** showed clearly defined cross peaks between 3-H and nonequivalent protons on $C^{3'}$, indicating that these protons are spatially close to each other. This is possible when 3-H and $C^{3'}$ are located at the same side of the cyclopropane ring plane. Owing to overlap of the 3-H signal and downfield signal of the *AB* system on $C^{3'}$, no reliable assignment could be made for compound **Vc** on the basis of the NOESY data. Nevertheless, taking into account similar spectral parameters of protons and carbon atoms neighboring to the spiro-carbon atom, compounds **Vb**, **Vc**, **VIIe**, and **VIIf** may be assumed to have the same configuration. No cross peaks between 3-H and nonequivalent protons on $C^{3'}$ were observed in the NOESY spectra of compounds **Va** and **VIIb** in DMSO-d_6 or $CDCl_3$. Presumably, their molecules are characterized by the opposite orientation of the spiro-fused rings, where the 3-H proton and $C^{3'}$ carbon atom are located at opposite sides of the cyclopropane ring plane.

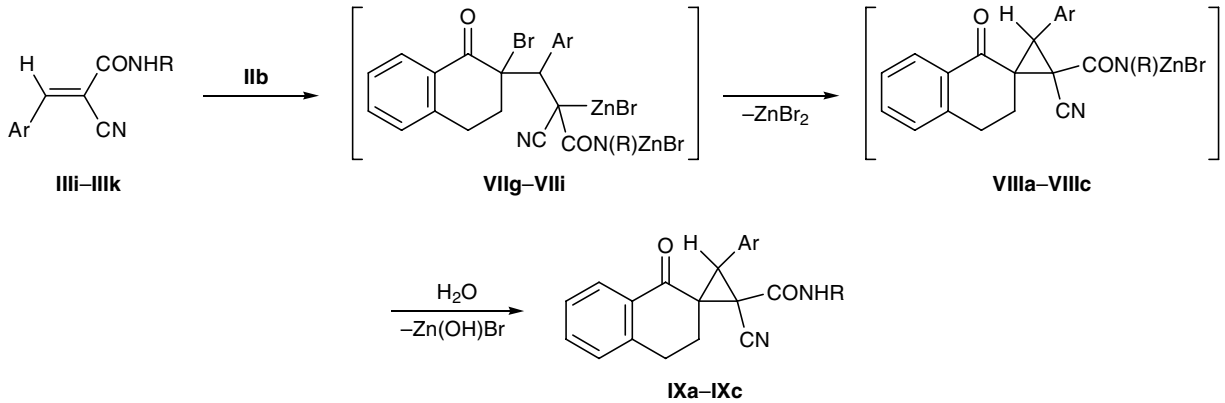
Zinc enolate **IIb** obtained from 2,2-dibromo-1,2,3,4-tetrahydronaphthalen-1-one was also brought into reactions with N-substituted 3-aryl-2-cyanoprop-2-enamides **IIIi**–**IIIk** (Scheme 2). The reaction was regioselective: attack by zinc enolate **IIb** on the C^3 atom in electrophile **IIIi**–**IIIk** gave intermediate adducts **VIIg**–**VIIi** whose spontaneous cyclization afforded cyclopropane derivatives **VIIIa**–**VIIIc**; hydrolysis of the latter led to the formation of N-substituted 3-aryl-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro-[cyclopropane-1,2′-naphthalene]-2-carboxamides **IXa**–**IXc**. Compounds **IXa**–**IXc** displayed in the IR spectra absorption bands at 1655 (C=O, amide), 1680 (C=O, ketone), 2210 (C≡N), and 3300 cm^{-1} (N–H). Their ^1H NMR spectra contained singlets from the 3-H proton at δ 3.69–3.78 ppm. The presence of only one set of signals indicates that amides **IXa**–**IXc** are formed as a single diastereoisomer; however, its steric configuration was not determined.

EXPERIMENTAL

The IR spectra were recorded from samples dispersed in mineral oil on UR-20 (**Vb**–**Vd**) and Specord 75IR spectrometers (**Va**, **VIIa**–**VIIf**, **IXa**–**IXc**). The ^1H and ^{13}C NMR spectra (including COSY, NOESY, HSQC, and HMBC experiments) were measured on a Bruker DRX-400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) from solutions in DMSO-d_6 (**Va**, **VIIb**) or $CDCl_3$ (**Vb**, **Vc**, **VIIe**, **VIIf**) using tetramethylsilane as internal reference. The ^1H NMR spectra of the other compounds were recorded on Bruker DRX-500 (500 MHz, DMSO-d_6, TMS; **Vd**), Mercury Plus-300 (300 MHz, HMDS; **IXa**: DMSO-d_6; **IXc**, $CDCl_3$), and Tesla BS-567 instruments (100 MHz, $CDCl_3$, HMDS, **IXb**).

3-(4-Chlorophenyl)-1′-oxo-1′,3′-dihydrospiro-[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (Va). 2,2-Dibromoindan-1-one, 0.013 mol, and 2-(4-chlorobenzylidene)malononitrile, 0.01 mol, were added to a mixture of 0.9 g of zinc (prepared as fine turnings), 8 ml of diethyl ether, and 5 ml of ethyl acetate, and the mixture was heated under reflux until the zinc dissolved almost completely. The mixture was then heated under reflux for an additional 40 min, cooled, treated with 5% acetic acid, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated,

Scheme 2.



IIIi, **VIg**, **VIIIa**, **IXa**, R = $PhCH_2$, Ar = Ph; **IIIj**, **VIh**, **VIIIb**, **IXb**, R = $PhCH_2$, Ar = 4-BrC_6H_4; **IIIk**, **VIi**, **VIIIc**, **IXc**, R = *cyclo*-C_6H_{11}, Ar = 4-ClC_6H_4.

and the residue was recrystallized from ethyl acetate. Yield 66%, mp 212–213°C. IR spectrum, ν, cm^{-1}: 1700, 2230. ^1H NMR spectrum, δ, ppm: 3.31 d (1H, 3′-H_B, J = 18.0 Hz), 3.40 d (1H, 3′-H_A, J = 18.0 Hz), 3.92 s (1H, 3-H), 7.53 d (2H, 3″-H, 5″-H, J = 8.8 Hz), 7.56 t (1H, 6′-H, J = 7.6 Hz), 7.60 d (2H, 2″-H, 6″-H, J = 8.8 Hz), 7.71 d (1H, 4′-H, J = 7.6 Hz), 7.79 t.d (1H, 5′-H, J = 7.6, 1.4 Hz), 7.84 d.d (1H, 7′-H, J = 7.6, 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 18.68 (C^2), 29.91 ($C^{3'}$), 38.98 (C^3), 45.01 (C^1), 112.27 (CN), 112.56 (CN), 123.67 ($C^{7'}$), 126.72 ($C^{4'}$), 128.09 ($C^{6'}$), 128.79 ($C^{3''}$, $C^{5''}$), 128.92 ($C^{1''}$), 131.65 ($C^{2''}$, $C^{6''}$), 133.62 ($C^{4''}$), 134.91 ($C^{7a'}$), 135.66 ($C^{5'}$), 151.81 ($C^{3a'}$), 195.29 ($C^{1'}$). Found, %: C 71.50; H 3.38; N 8.70. $C_{19}H_{11}ClN_2O$. Calculated, %: C 71.59; H 3.48; N 8.79.

Compounds **Vb**–**Vd** were synthesized in a similar way.

Methyl 3-(4-bromophenyl)-2-cyano-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2-carboxylate (Vb). Yield 67%, mp 168–169°C. IR spectrum, ν, cm^{-1}: 1710, 1745, 2230. ^1H NMR spectrum, δ, ppm: 3.39 d (1H, 3′-H_B, J = 18.3 Hz), 3.51 d (1H, 3′-H_A, J = 18.3 Hz), 3.78 s (1H, 3-H), 3.95 s (3H, OMe), 7.12 d (2H, *o*-H, J = 8.5 Hz), 7.45 m (3H, *m*-H, 6′-H), 7.52 d.d.t (1H, 4′-H, J = 7.7, 1.8, 0.9 Hz), 7.68 t.d (1H, 5′-H, J = 7.5, 1.3 Hz), 7.77 d.d (1H, 7′-H, J = 7.7, 1.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 31.95 (C^2), 34.74 ($C^{3'}$), 41.54 (C^3), 46.01 (C^1), 54.24 (OMe), 112.72 (CN), 122.36 (C^p), 124.24 ($C^{7'}$), 126.02 ($C^{4'}$), 128.13 ($C^{6'}$), 128.84 (C^i), 131.07 (C^o), 131.72 (C^m), 135.44 ($C^{5'}$), 136.74 ($C^{7a'}$), 150.60 ($C^{3a'}$), 165.86 (COO), 194.22 ($C^{1'}$). Found, %: C 60.60; H 3.50; N 3.48. $C_{20}H_{14}BrNO_3$. Calculated, %: C 60.62; H 3.56; N 3.53.

Methyl 2-cyano-3-(2,4-dichlorophenyl)-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2-carboxylate (Vc). Yield 66%, mp 153–154°C. IR spectrum, ν, cm^{-1}: 1710, 1745, 2230. ^1H NMR spectrum, δ, ppm: 3.40 d (1H, 3′-H_B, J = 18.5 Hz), 3.59 d (1H, 3′-H_A, J = 18.5 Hz), 3.61 d (1H, 3-H, ^4J = 1.0 Hz), 3.97 s (3H, OMe), 7.35–7.32 m (2H, 3″-H, 5″-H), 7.43 d.d (1H, 6′-H, J = 7.7, 7.3 Hz), 7.52 d.m (1H, 4′-H, J = 7.7 Hz), 7.57 d.t (1H, 6″-H, J = 7.8, 1.0 Hz), 7.66 d.d.d (1H, 5′-H, J = 7.7, 7.3, 1.2 Hz), 7.76 d.d.d (1H, 7′-H, J = 7.7, 1.2, 0.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 31.80 (C^2), 33.99 ($C^{3'}$), 39.27 (C^3), 46.48 (C^1), 54.33 (OMe), 112.79 (CN), 124.29 ($C^{7'}$), 125.89 ($C^{4'}$), 127.34 ($C^{1''}$), 127.41 ($C^{5''}$), 128.07 ($C^{6'}$), 129.42 ($C^{3''}$), 131.37 ($C^{6''}$), 134.88 ($C^{4''}$ or $C^{2''}$), 135.27 ($C^{5'}$), 135.45 ($C^{2''}$ or $C^{4''}$), 136.36 ($C^{7a'}$), 150.77 ($C^{3a'}$), 165.67 (COO), 193.85 ($C^{1'}$). Found, %: C 62.10; H 3.35; N 3.61. $C_{20}H_{13}Cl_2NO_3$. Calculated, %: C 62.19; H 3.39; N 3.63.

Ethyl 2-cyano-3-(2,4-dichlorophenyl)-1′-oxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2-carboxylate (Vd). Yield 67%, mp 170–172°C. IR spectrum, ν, cm^{-1}: 1710, 1745, 2230. ^1H NMR spectrum, δ, ppm: 1.31 t (3H, CH_3), 3.54 s (2H, CH_2), 3.70 s (1H, CH), 4.33 q (2H, C**H**$_2$CH$_3$), 7.45–7.77 m (7H, C_6H_4, 2,4-$Cl_2C_6H_3$). Found, %: C 62.95; H 3.73; N 3.46. $C_{21}H_{15}Cl_2NO_3$. Calculated, %: C 63.02; H 3.78; N 3.50.

3-Aryl-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitriles VIIa–VIId (*general procedure*)**.** 2,2-Dibromo-1,2,3,4-tetrahydronaphthalen-1-one, 0.024 mol, was added to a mixture of 2 g of zinc (prepared as fine turnings), 7 ml of diethyl ether, and 10 ml of ethyl acetate. The mixture was heated to initiate the reaction which then occurred spontaneously. When the reaction was complete, the mixture was heated for 5 min under reflux and cooled, the liquid phase was separated by decanting and transferred into a flask containing 0.02 mol of 2-arylmethylidenemalononitrile, and the mixture was heated for 60 min under reflux. It was then cooled, treated with 5% acetic acid, and extracted with diethyl ether, the extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from ethyl acetate.

1′-Oxo-3-phenyl-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitrile (VIIa). Yield 67%, mp 198–200°C. IR spectrum, ν, cm^{-1}: 1685, 2230. ^1H NMR spectrum, δ, ppm: 1.70 m (1H, 3′-H_B), 2.67 m (1H, 3′-H_A), 2.82 d.t (1H, 4′-H_B), 3.08 m (1H, 4′-H_A), 4.19 s (1H, 3-H), 7.20–7.90 m (9H, C_6H_5, C_6H_4). Found, %: C 80.47; H 4.69; N 9.35. $C_{20}H_{14}N_2O$. Calculated, %: C 80.52; H 4.73; N 9.39.

3-(4-Chlorophenyl)-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitrile (VIIb). Yield 65%, mp 193–194°C. IR spectrum, ν, cm^{-1}: 1680, 2220. ^1H NMR spectrum, δ, ppm: 1.68 d.t (1H, 3′-H_B, J = 14.7, 4.3 Hz), 2.75 d.d.d (1H, 3′-H_A, J = 14.7, 12.0, 4.3 Hz), 3.08 d.t (1H, 4′-H_B, J = 16.5, 4.3 Hz), 3.23 d.d.d (1H, 4′-H_A, J = 16.5, 12.0, 4.3 Hz), 4.24 s (1H, 3-H), 7.46 d (1H, 5′-H, J = 7.5 Hz), 7.48 t (1H, 7′-H, J = 7.5 Hz), 7.53 d (2H, *m*-H, J = 8.8 Hz), 7.63 d (2H, *o*-H, J = 8.8 Hz), 7.70 t.d (1H, 6′-H, J = 7.5, 1.4 Hz), 8.03 d.d (1H, 8′-H, J = 7.5, 1.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.20 (C^2), 25.23 ($C^{3'}$), 25.81 ($C^{4'}$), 38.41 (C^3), 44.53 (C^1),

112.19 (CN), 112.99 (CN), 127.19 ($C^{7'}$), 127.46 ($C^{8'}$), 128.32 (C^{i}), 128.83 (C^{m}), 129.21 ($C^{5'}$), 130.94 ($C^{8a'}$), 131.87 (C^{o}), 133.49 (C^{p}), 134.81 ($C^{6'}$), 144.05 ($C^{4a'}$), 187.94 ($C^{1'}$). Found, %: C 72.10; H 3.89; N 8.38. $C_{20}H_{13}ClN_2O$. Calculated, %: C 72.18; H 3.94; N 8.42.

3-(3-Bromophenyl)-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitrile (VIIc). Yield 62%, mp 211–213°C. IR spectrum, ν, cm^{-1}: 1670, 2230. ^1H NMR spectrum, δ, ppm: 1.62 m (1H, 3′-H_B), 2.79 m (1H, 3′-H_A), 3.07 m (1H, 4′-H_B), 3.21 m (1H, 4′-H_A), 4.26 s (1H, 3-H), 7.39–8.02 m (8H, C_6H_4, BrC_6H_4). Found, %: C 63.65; H 3.42; N 7.40. $C_{20}H_{13}BrN_2O$. Calculated, %: C 63.68; H 3.47; N 7.43.

3-(3,4-Dimethoxyphenyl)-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2,2-dicarbonitrile (VIId). Yield 68%, mp 186–187°C. IR spectrum, ν, cm^{-1}: 1670, 2220. ^1H NMR spectrum, δ, ppm: 1.71 m (1H, 3′-H_B), 2.79 m (1H, 3′-H_A), 3.08 m (1H, 4′-H_B), 3.20 m (1H, 4′-H_A), 3.75 s (3H, CH_3O), 3.77 s (3H, CH_3O), 4.13 s (1H, 3-H), 6.83–8.02 m (7H, C_6H_4, C_6H_3). Found, %: C 73.70; H 4.98; N 7.79. $C_{22}H_{18}N_2O_2$. Calculated, %: C 73.73; H 5.06; N 7.82.

Compounds **VIIe** and **VIIf** were synthesized in a similar way.

Methyl 3-(4-bromophenyl)-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxylate (VIIe). Yield 66%, mp 222–223°C. IR spectrum, ν, cm^{-1}: 1680, 1725, 2210. ^1H NMR spectrum, δ, ppm: 2.32 d.t (1H, 3′-H_B, J = 13.7, 5.1 Hz), 2.38 d.d.d (1H, 3′-H_A, J = 13.7, 9.9, 4.3 Hz), 3.05 d.t (1H, 4′-H_B, J = 16.5, 4.8 Hz), 3.19 d.d.d (1H, 4′-H_A, J = 16.5, 10.0, 5.0 Hz), 3.60 s (1H, 3-H), 3.94 s (3H, OMe), 7.04 d (2H, *o*-H, J = 8.6 Hz), 7.37–7.31 m (2H, 7′-H, 5′-H), 7.40 d (2H, *m*-H, J = 8.6 Hz), 7.55 t.d (1H, 6′-H, J = 7.5, 1.5 Hz), 7.97 d.d (1H, 8′-H, J = 7.9, 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.00 and 28.14 ($C^{4'}$, $C^{3'}$), 31.43 (C^{2}), 41.03 (C^{3}), 45.93 (C^{1}), 54.31 (OMe), 114.26 (CN), 122.16 (C^{p}), 127.44 ($C^{7'}$), 128.31 ($C^{8'}$), 128.50 ($C^{5'}$), 129.85 (C^{i}), 130.81 (C^{o}), 131.80 (C^{m}), 132.90 ($C^{8a'}$), 134.31 ($C^{6'}$), 142.60 ($C^{4a'}$), 165.41 (COO), 188.65 ($C^{1'}$). Found, %: C 61.40; H 3.87; N 3.38. $C_{21}H_{16}BrNO_3$. Calculated, %: C 61.48; H 3.93; N 3.41.

Methyl 2-cyano-3-(2,4-dichlorophenyl)-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxylate (VIIf). Yield 63%, mp 159–160°C. IR spectrum, ν, cm^{-1}: 1680, 1725, 2210. ^1H NMR spectrum, δ, ppm: 2.34 d.d.d (1H, 3′-H_B, J = 14.4, 6.8, 4.2 Hz), 2.67 d.d.d (1H, 3′-H_A, J = 14.4, 9.7, 4.3 Hz), 2.94 d.d.d (1H, 4′-H_B, J = 16.4, 6.8, 4.3 Hz), 3.13 d.d.d (1H, 4′-H_A, J = 16.4, 6.8, 4.3 Hz), 3.42 d (1H, 3-H, ^4J = 1.1 Hz), 3.96 s (3H, OCH_3), 7.35–7.27 m (3H, 7′-H, 5″-H, 5′-H), 7.38 d (1H, 3″-H, J = 2.1 Hz), 7.46 d.d (1H, 6″-H, J = 8.4, 1.1 Hz), 7.53 t.d (1H, 6′-H, J = 7.5, 1.5 Hz), 7.97 d.d (1H, 8′-H, J = 7.9, 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.46 and 27.48 ($C^{4'}$, $C^{3'}$), 31.77 (C^{2}), 39.72 (C^{3}), 45.93 (C^{1}), 54.38 (OMe), 114.09 (CN), 127.32, 127.38 ($C^{7'}$, $C^{5''}$), 128.26 ($C^{8'}$), 128.40 ($C^{5'}$), 128.64 ($C^{1''}$), 129.36 ($C^{3''}$), 130.71 ($C^{6''}$), 132.51 ($C^{8a'}$), 134.21 ($C^{6'}$), 134.50 ($C^{4''}$), 135.12 ($C^{2''}$), 142.81 ($C^{4a'}$), 165.17 (COO), 188.10 ($C^{1'}$). Found, %: C 62.98; H 3.69; N 3.38. $C_{21}H_{15}Cl_2NO_3$. Calculated, %: C 63.02; H 3.78; N 3.50.

N-Substituted 3-aryl-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxamides IXa–IXc (*general procedure*)**.** A solution of 0.025 mol of 2,2-dibromo-1,2,3,4-tetrahydronaphthalen-1-one in 3 ml of ethyl acetate was added to a mixture of 4 g of zinc (prepared as fine turnings), 8 ml of diethyl ether, and 5 ml of ethyl acetate. The mixture was heated to initiate the reaction which then occurred spontaneously. When the reaction was complete, the mixture was heated for 10 min under reflux and cooled, and the liquid phase was separated by decanting. N-Substituted 3-aryl-2-cyanoprop-2-enamide, 0.01 mol, was added to the liquid phase, and the mixture was heated for 60 min, cooled, treated with a solution of acetic acid, and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated, and the residue was recrystallized from methanol.

***N*-Benzyl-2-cyano-1′-oxo-3-phenyl-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxamide (IXa).** Yield 51%, mp 216–217°C. IR spectrum, ν, cm^{-1}: 1660–1670, 2210. ^1H NMR spectrum, δ, ppm: 1.75 m (1H, 3′-H_B), 2.29 m (1H, 3′-H_A), 3.02 m (1H, 4′-H_B), 3.20 m (1H, 4′-H_A), 3.58 s (1H, 3-H), 4.39 m (2H, C**H**$_2$Ph), 7.09–7.78 m (14H, C_6H_5, C_6H_4), 9.42 t (1H, NH, J = 5.4 Hz). Found, %: C 79.75; H 5.40; N 6.84. $C_{27}H_{22}N_2O_2$. Calculated, %: C 79.78; H 5.46; N 6.89.

***N*-Benzyl-3-(4-bromophenyl)-2-cyano-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxamide (IXb).** Yield 56%, mp 211–212°C. IR spectrum, ν, cm^{-1}: 1660, 1680, 2210, 3370. ^1H NMR spectrum, δ, ppm: 2.21 m (2H, 3′-H, 4′-H), 2.98 m (2H, 3′-H, 4′-H), 3.69 s (1H, CH), 4.48 m (2H, C**H**$_2$Ph), 6.79–7.65 m (13H, C_6H_4, BrC_6H_4, C_6H_5, NH). Found, %: C 66.75; H 4.30; N 5.70. $C_{27}H_{21}BrN_2O_2$. Calculated, %: C 66.81; H 4.36; N 5.77.

3-(4-Chlorophenyl)-2-cyano-*N*-cyclohexyl-1′-oxo-3′,4′-dihydro-1′*H*-spiro[cyclopropane-1,2′-naphthalene]-2-carboxamide (IXc). Yield 54%, mp 205–206°C. IR spectrum, ν, cm^{-1}: 1655, 1680, 2210, 3300. ^1H NMR spectrum, δ, ppm: 1.10–2.05 m [10H, $(CH_2)_5$]; 2.34 m (2H), 3.02 m (1H), and 3.09 m (1H) (3′-H, 4′-H); 3.78 s (1H, CH); 3.81 m (1H, NCH); 6.57 d (1H, NH); 7.02–7.94 m (8H, C_6H_4, 4-ClC_6H_4). Found, %: C 72.08; H 5.80; N 6.42. $C_{26}H_{25}ClN_2O_2$. Calculated, %: C 72.13; H 5.82; N 6.47.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 07-03-96035).

REFERENCES

1. Shchepin, V.V., Silaichev, P.S., and Vakhrin, M.I., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 1598.
2. Shchepin, V.V., Silaichev, P.S., Stepanyan, Yu.G., Lebedev, K.P., and Vakhrin, M.I., *Russ. J. Gen. Chem.*, 2006, vol. 76, p. 743.