

# Cyclopropanation of N-Substituted 2-Oxochromene- and 6-Bromo-2-oxochromene-3-carboxamides with Zinc Enolates Derived from 1-Aryl-2,2-dibromoalkanones

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**Abstract**—Zinc enolates derived from 1-aryl-2,2-dibromoalkanones react with *N*-cyclohexyl-2-oxochromene-3-carboxamides to give *N*-cyclohexyl-1-alkyl-1-aryloxy-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamides mainly as *cis* isomers with respect to the substituents in positions 1 and 1a. Reactions of the same zinc enolates with *N*-benzyl-2-oxochromene-3-carboxamide and *N*-benzyl-6-bromo-2-oxochromene-3-carboxamide lead to formation of 1-aryl-2-benzyl- and 1-aryl-2-benzyl-6-bromo-1-hydroxy-9c-alkyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-diones. The reaction of zinc enolates with *N*-aryl-2-oxochromene-3-carboxamides in a weakly polar solvent (diethyl ether or ethyl acetate) affords mixtures of *cis*-*N*-aryl-1-aryloxy-1-alkyl-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamides and their cyclic isomers, 9c-alkyl-1,2-diaryloxy-1-hydroxy-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-diones, the latter prevailing. *N*-Substituted 1-alkyl-1-aryloxy-1-alkyl-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamides in which the aryl group on C<sup>1</sup> and the carboxamide group on C<sup>1a</sup> are arranged *trans* are formed by reactions of zinc enolates with the corresponding 2-oxochromene-3-carboxamides in the presence of hexamethylphosphoric triamide.

We previously showed that alkyl 2-oxochromene-3-carboxylates readily react with bromine-containing zinc enolates in diethyl ether–ethyl acetate to give 2-oxochromene derivatives with a fused cyclopropane fragment [1, 2].

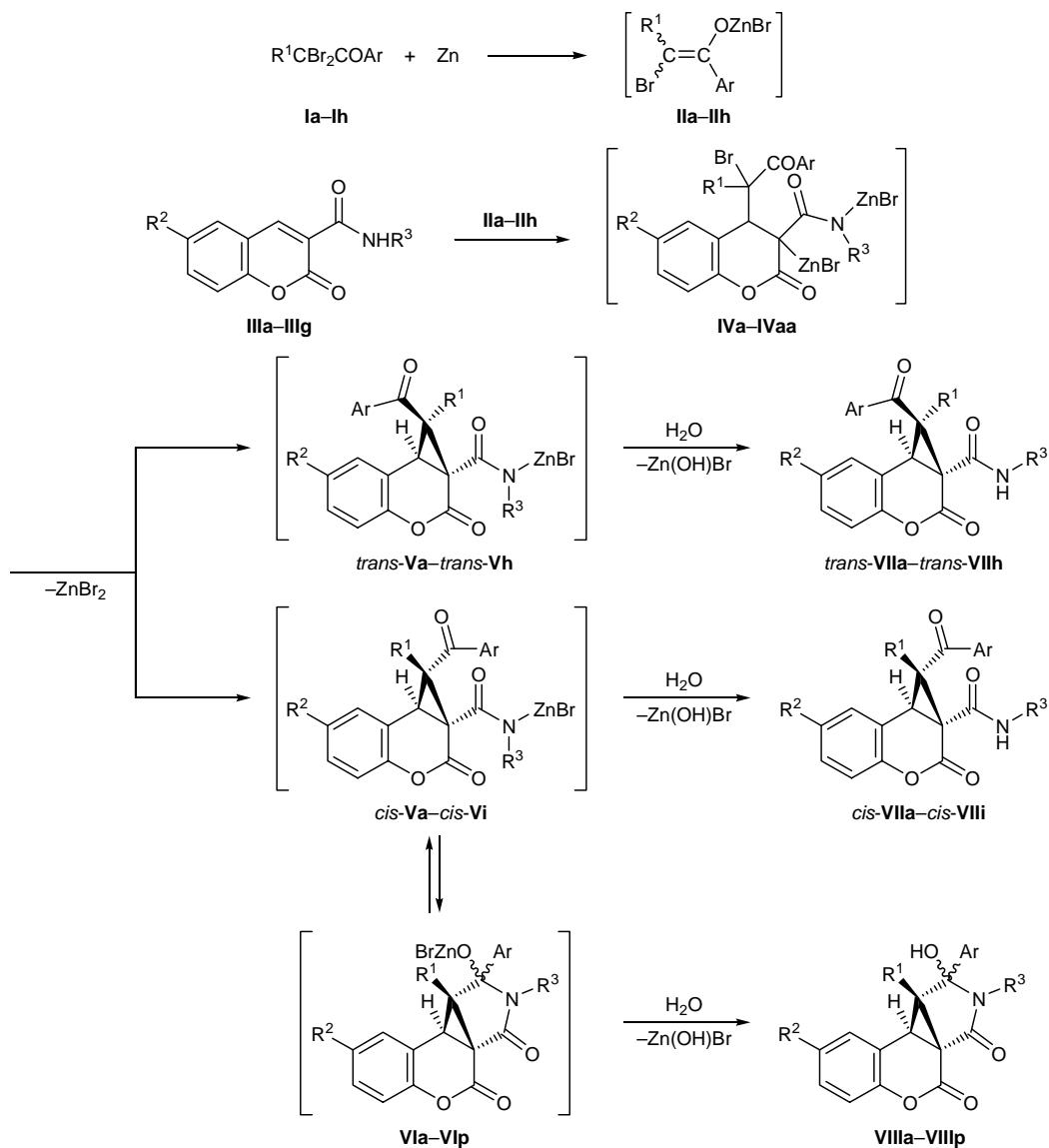
The goal of the present study was to elucidate the possibility for cyclopropanation of *N*-cyclohexyl-, *N*-benzyl-, *N*-benzyl-6-bromo-, and *N*-aryl-2-oxochromene-3-carboxamides **IIIa**–**IIIg** with bromine-containing zinc enolates **IIa**–**IIh** obtained from  $\alpha,\alpha$ -dibromo ketones **Ia**–**Ih**. Taking into account the presence of a labile amide hydrogen atom which should be replaced first by ZnBr group by the action of zinc enolate, we anticipated reduced electrophilicity of the double bond in the substrate and formation of insoluble salt-like materials which should hamper the process. In fact, insoluble materials were formed in the reactions of zinc enolates **IIa**–**IIh** with *N*-benzyl-6-bromo-2-oxochromene-3-carboxamide (**IIIc**) at a ratio of 2:1. We succeeded in avoiding precipitation of salt-like products by carrying out the reactions at a **II**-to-**III** ratio of 3:1. Under these conditions, the reactions of

zinc enolates **IIa**–**IIh** with *N*-substituted carboxamides **IIIa**–**IIIg** followed Scheme 1.

Attack by zinc enolate **IIa**–**IIh** on the electrophilic C<sup>4</sup> atom in substrate **IIIa**–**IIIg** afforded intermediate **IV** which underwent spontaneous cyclization to isomeric structures *trans*-**V** and *cis*-**V** having a fused cyclopropane ring. The aryl group and the amide moiety in the *trans* isomer are located at opposite sides with respect to the cyclopropane ring plane, while in the *cis* isomer these fragments appear at the same side. Hydrolysis of intermediates *trans*-**V** and *cis*-**V** should give the corresponding *trans* and *cis* isomers *trans*-**VIIa**–*trans*-**VIIh** and *cis*-**VIIa**–*cis*-**VIIe**. In the reactions of zinc enolates **IIb**–**IId**, **IIf**, and **IIg** with *N*-cyclohexyl-2-oxochromene-3-carboxamide **IIIa** we obtained *N*-cyclohexyl-1-alkyl-1-aryloxy-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamides *cis*-**VIIa**–*cis*-**VIIe**. Their structure was proved by the analytical data and IR and <sup>1</sup>H NMR spectra.

The IR spectra of *cis*-**VIIa**–*cis*-**VIIe** contained absorption bands typical of stretching vibrations of the amide and ketone carbonyl groups (1660–1680 cm<sup>−1</sup>),

Scheme 1.



**I, II,**  $\text{R}^1 = \text{Me}, \text{Ar} = \text{Ph}$  (**a**),  $4\text{-FC}_6\text{H}_4$  (**b**),  $4\text{-ClC}_6\text{H}_4$  (**c**),  $4\text{-BrC}_6\text{H}_4$  (**d**),  $4\text{-MeC}_6\text{H}_4$  (**e**);  $\text{R}^1 = \text{Et}, \text{Ar} = \text{Ph}$  (**f**),  $4\text{-ClC}_6\text{H}_4$  (**g**),  $4\text{-BrC}_6\text{H}_4$  (**h**); **III**,  $\text{R}^2 = \text{H}, \text{R}^3 = \text{cyclo-C}_6\text{H}_{11}$  (**a**),  $\text{CH}_2\text{Ph}$  (**b**),  $\text{Ph}$  (**d**),  $4\text{-MeC}_6\text{H}_4$  (**e**),  $4\text{-MeOC}_6\text{H}_4$  (**f**),  $2\text{-MeOC}_6\text{H}_4$  (**g**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}$  (**c**); **IV**,  $\text{R}^2 = \text{H}, \text{R}^3 = \text{cyclo-C}_6\text{H}_{11}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-FC}_6\text{H}_4$  (**a**),  $4\text{-ClC}_6\text{H}_4$  (**b**),  $4\text{-BrC}_6\text{H}_4$  (**c**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{cyclo-C}_6\text{H}_{11}, \text{R}^1 = \text{Et}, \text{Ar} = \text{Ph}$  (**d**),  $4\text{-ClC}_6\text{H}_4$  (**e**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**f**),  $4\text{-BrC}_6\text{H}_4$  (**g**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = \text{Ph}$  (**h**),  $4\text{-ClC}_6\text{H}_4$  (**i**),  $4\text{-BrC}_6\text{H}_4$  (**j**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Et}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**k**),  $4\text{-BrC}_6\text{H}_4$  (**l**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**m**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}, \text{R}^1 = \text{Et}, \text{Ar} = \text{Ph}$  (**n**),  $4\text{-ClC}_6\text{H}_4$  (**o**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-MeC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = \text{Ph}$  (**p**),  $4\text{-MeC}_6\text{H}_4$  (**q**),  $4\text{-FC}_6\text{H}_4$  (**r**),  $4\text{-ClC}_6\text{H}_4$  (**s**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-MeC}_6\text{H}_4, \text{R}^1 = \text{Et}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**t**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-BrC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-FC}_6\text{H}_4$  (**u**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-BrC}_6\text{H}_4, \text{R}^1 = \text{Et}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**v**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-MeOC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**w**),  $4\text{-BrC}_6\text{H}_4$  (**x**);  $\text{R}^2 = \text{H}, \text{R}^3 = 2\text{-MeOC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-MeC}_6\text{H}_4$  (**y**),  $4\text{-ClC}_6\text{H}_4$  (**z**),  $4\text{-BrC}_6\text{H}_4$  (**aa**); **trans--V, trans--VII**,  $\text{R}^2 = \text{H}, \text{R}^3 = \text{cyclo-C}_6\text{H}_{11}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**a**); **cis--V, cis--VII**,  $\text{R}^2 = \text{H}, \text{R}^3 = \text{C}_6\text{H}_{11}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-FC}_6\text{H}_4$  (**a**),  $4\text{-ClC}_6\text{H}_4$  (**b**),  $4\text{-BrC}_6\text{H}_4$  (**c**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{C}_6\text{H}_{11}, \text{R}^1 = \text{Et}, \text{Ar} = \text{Ph}$  (**d**),  $4\text{-ClC}_6\text{H}_4$  (**e**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**f**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-BrC}_6\text{H}_4, \text{R}^1 = \text{Et}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**g**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-MeOC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**h**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**i**); **VII, VIII**,  $\text{R}^2 = \text{H}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**a**),  $4\text{-BrC}_6\text{H}_4$  (**b**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**c**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Et}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**d**),  $4\text{-BrC}_6\text{H}_4$  (**e**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}, \text{R}^1 = \text{Et}, \text{Ar} = \text{Ph}$  (**f**),  $4\text{-ClC}_6\text{H}_4$  (**g**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-MeC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**h**);  $\text{R}^2 = \text{H}, \text{R}^3 = 2\text{-MeOC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**i**); **VII, VIII**,  $\text{R}^2 = \text{H}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**a**),  $4\text{-BrC}_6\text{H}_4$  (**b**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**c**);  $\text{R}^2 = \text{Br}, \text{R}^3 = \text{CH}_2\text{Ph}, \text{R}^1 = \text{Et}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**d**),  $4\text{-BrC}_6\text{H}_4$  (**e**);  $\text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}, \text{R}^1 = \text{Et}, \text{Ar} = \text{Ph}$  (**f**),  $4\text{-ClC}_6\text{H}_4$  (**g**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-MeC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**h**);  $\text{R}^2 = \text{H}, \text{R}^3 = 4\text{-BrC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-ClC}_6\text{H}_4$  (**i**); **VII, VIII**,  $\text{R}^2 = \text{H}, \text{R}^3 = 2\text{-MeOC}_6\text{H}_4, \text{R}^1 = \text{Me}, \text{Ar} = 4\text{-MeC}_6\text{H}_4$  (**n**),  $4\text{-ClC}_6\text{H}_4$  (**o**),  $4\text{-BrC}_6\text{H}_4$  (**p**).

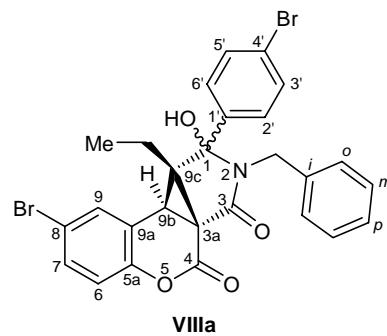
lactone carbonyl ( $1730\text{ cm}^{-1}$ ), and N–H bond ( $3360\text{--}3370\text{ cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectra of amides *cis*-**VIIa–*cis*-**VIIc** we observed singlets at  $\delta$   $3.70\text{--}3.93$ ,  $1.13\text{--}1.20$ , and  $8.23\text{--}8.24$  ppm, which belong to the  $7\text{b}$ -H proton, protons of the methyl group, and NH proton, respectively. Compounds *cis*-**VIIId** and *cis*-**VIIe** characteristically showed in the  $^1\text{H}$  NMR spectra a downfield triplet at  $\delta$   $0.45\text{--}0.57$  ppm due to methyl protons of the ethyl group on C<sup>1</sup>. The obtained data indicate that compounds *cis*-**VIIa–*cis*-**VIIe** are formed as a single isomer with respect to junction of the cyclopropane and dihydropyran rings. We recently showed that structurally related 1-alkyl-1-aryl-6-bromo-1*a*-piperidinocarbonyl- and -1*a*-morpholinocarbonyl-1*a*,7*b*-dihydrocyclopropa[*c*]chromen-2-ones (which were prepared by reactions of bromine-containing zinc enolates with 6-bromo-2-oxochromene-3-carboxylic acid piperide and morpholide, respectively) were formed as a single isomer with *cis*-junction of the cyclopropane and dihydropyran rings [3]. Their  $^1\text{H}$  NMR spectra contained a singlet at  $\delta$   $1.10\text{--}1.17$  ppm (1-methyl derivatives) or a triplet at  $\delta$   $0.45$  ppm (1-ethyl derivatives). Insofar as compounds *cis*-**VIIa–*cis*-**VIIe** had similar spectral parameters, they were assigned the same configuration, i.e., with *cis*-fused cyclopropane and dihydropyran rings. In the  $^1\text{H}$  NMR spectrum of 1-(4-bromobenzoyl)-*N*-cyclohexyl-1-methyl-2-oxo-1*a*,7*b*-dihydrocyclopropa[*c*]chromene-1*a*-carboxamide (**VIIc**) signals from both *cis* (major) and *trans* isomer (minor) were present.******

Zinc enolates **IIc**, **IIId**, and **IIIf**–**IIH** reacted with *N*-benzyl- and *N*-benzyl-6-bromo-2-oxochromene-3-carboxamides **IIIb** and **IIIc** in a regioselective fashion to give intermediates **IV** which underwent stereoselective cyclization to the corresponding cyclopropane derivatives *cis*-**V**. The *cis* arrangement of the aryl and carboxamide fragments in *cis*-**V** favors intramolecular ring closure to isomeric structures **VIIa**–**VIIe**; hydrolysis of the latter leads to 1-aryl-2-benzyl- and 1-aryl-2-benzyl-6-bromo-1-hydroxy-9*c*-alkyl-1,2,9*b*,9*c*-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-diones **VIIia**–**VIIie** (Scheme 1).

The structure of compounds **VIIia**–**VIIie** was confirmed by the analytical data and IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Their IR spectra contained absorption bands corresponding to stretching vibrations of the lactam carbonyl ( $1660\text{--}1665\text{ cm}^{-1}$ ), lactone carbonyl ( $1750\text{--}1760\text{ cm}^{-1}$ ), and OH group ( $3200\text{--}3320\text{ cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectra we observed signals at  $\delta$   $3.50\text{--}3.60$  ppm due to 9*b*-H and two doublets at  $\delta$   $3.69\text{--}3.80$  and  $4.27\text{--}4.31$  ppm ( $J = 15.5\text{ Hz}$ ) due to methylene

protons in the benzyl group. The singlet from the methyl group on C<sup>9c</sup> in the spectra of **VIIia**–**VIIic** appears in a stronger field ( $\delta$   $0.51\text{--}0.61$  ppm) relative to the corresponding signal of *cis*-**VIIa–*cis*-**VIIc**.**

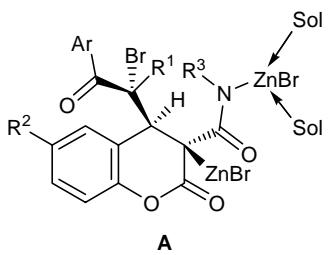
Signals in the  $^{13}\text{C}$  NMR spectrum of 2-benzyl-8-bromo-1-(4-bromophenyl)-9*c*-ethyl-1-hydroxy-1,2,9*b*,9*c*-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-dione (**VIIie**) were assigned using two-dimensional  $^{13}\text{C}$ – $^1\text{H}$  HETCOR and  $^1\text{H}$ – $^{13}\text{C}$  HMBC techniques. The cyclopropane fragment gives rise to signals at  $\delta_{\text{C}}$   $33.22$  (C<sup>9b</sup>),  $36.76$  (C<sup>3a</sup>), and  $41.55$  ppm (C<sup>9c</sup>). Instead of signal from carbonyl carbon atom in the aryl fragment, typical of open structures ( $\delta_{\text{C}}$   $195$  ppm), a signal at  $\delta_{\text{C}}$   $92.06$  ppm is present; it belongs to the C<sup>1</sup> atom and is consistent with the cyclic structure of compound **VIIie**. In the 2D HMBC spectrum we observed cross peaks between C<sup>1</sup> and 9*b*-H, hydroxy proton, nonequivalent protons in the methylene groups at C<sup>9c</sup> and N<sup>2</sup>, and *ortho*-protons (2'-H and 6'-H) in the *p*-bromophenyl substituent.



We can conclude that reduction of steric hindrances in going from *N*-cyclohexyl to *N*-benzyl derivatives makes cyclic structures **VIIia**–**VIIie** more thermodynamically stable as compared to the corresponding isomers *cis*-**V**.

The reactions of zinc enolates **IIb**–**IIg** with *N*-aryl-2-oxochromene-3-carboxamides **IIIId**–**IIIg** in weakly polar aprotic solvents (diethyl ether and ethyl acetate) afforded mainly 9*c*-alkyl-1,2-diaryl-1-hydroxy-1,2,9*b*,9*c*-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-diones **VIIIf**–**VIIIp**. In some cases, the corresponding open *cis* isomers (*cis*-**VIIIf**–*cis*-**VIIi**) were also formed, their fraction attaining 45%. The ratio of isomers *cis*-**VII** and **VIII** depends on the solvent nature. For example, heating of compound **VIIIm** in DMSO to  $100^{\circ}\text{C}$  gave a  $\sim 1:1$  mixture of the initial cyclic compound ( $\delta$   $0.58$  ppm, s, 3H, 9*c*-Me) and its open isomer *cis*-**VII** ( $\delta$   $1.02$  ppm, s, 3H, 1-Me). In order to estimate the effect of the sol-

vent we examined reactions of zinc enolates **IIa–IId** and **IIg** with amides **IIIa** and **IIIc–IIIe** in diethyl ether, ethyl acetate, and HMPA. The presence of HMPA radically changes the stereoselectivity of the process which in this case involves *trans* intermediates **trans-V**; hydrolysis of the latter gives N-substituted 1-alkyl-1-aryl-2-oxo-1a,7b-dihydrocyclopropa[c]-chromene-1a-carboxamides **VIIa–VIIh** with *trans* arrangement of the aryl and carboxamide groups with respect to the cyclopropane ring. The corresponding *trans* isomers were obtained regardless of the initial zinc enolate (**IIa–IId**, **IIg**) and amide nature (**IIIa**, **IIIc–IIIe**). Presumably, solvation by HMPA molecules of the N–ZnBr fragment considerably increases its size. Therefore, the most favorable transition state for intermediates **trans-IVa–trans-IVh** is likely to be structure **A** where spatial interaction between the carboxamide and aryl fragments is minimized. As a result, amides **trans-VIIa–trans-VIIh** are formed.



The structure of amides **trans-VIIa–trans-VIIh** was proved by the data of IR and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectroscopy and elemental analysis. Their IR spectra contained absorption bands due to stretching vibrations of the ketone and lactone carbonyl groups (1660–1680 and 1725–1730  $\text{cm}^{-1}$ , respectively) and amide N–H bond (3315–3360  $\text{cm}^{-1}$ ). Signals at  $\delta$  1.58–1.71 and 3.60–3.71 ppm in the  $^1\text{H}$  NMR spectrum belong to the 1- $\text{CH}_3$  group and 7b-H, respectively, in **trans-VIIa–trans-VIIg**; protons of the ethyl group on C<sup>1</sup> in **trans-VIIh** give rise to signals at  $\delta$  0.88, 2.08, and 2.33 ppm. The  $^{13}\text{C}$  NMR spectrum of *N*-benzyl-1-benzoyl-6-bromo-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[c]-chromene-1a-carboxamide (**trans-VIIb**) contained signals at  $\delta_{\text{C}}$  34.79, 38.44, and 43.46 ppm, which correspond, respectively, to the C<sup>7b</sup>, C<sup>1a</sup>, and C<sup>1</sup> atoms; these signals indicate the presence of a cyclopropane fragment in molecule **trans-VIIb**. Also, a signal at  $\delta_{\text{C}}$  194.23 ppm was observed, which was assigned to the ketone carbonyl carbon atom. The *trans* orientation of the aryl and carboxamide groups was proved by measuring the stationary nuclear Overhauser effects in the 1D-difference NOE and 2D NOESY experiments.

In both cases, strong NOE was observed between 7b-H and protons of the methyl group on C<sup>1</sup>, indicating their *cis* arrangement with respect to the three-membered ring plane. No NOE was observed in compounds **VIIIe** and **VIIIm** where the 9b-H proton and alkyl group on C<sup>1</sup> are arranged *trans*.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The  $^1\text{H}$  NMR spectra of **trans-VIId**, **trans-VIIIf**, **trans-VIIh**, **cis-VIIa**, **cis-VIIe**, **VIIIc**, and **VIIId** were recorded on a Bruker DRX-500 instrument (500 MHz) from solutions in DMSO-*d*<sub>6</sub>–CCl<sub>4</sub> (1:3); of **trans-VIIa–trans-VIIc**, **VIIIe**, and **VIIIm**, on a Bruker DRX-400 instrument (400 MHz) from solutions in DMSO-*d*<sub>6</sub>; and of **cis-VIIa–cis-VIIe**, **VIIIa**, **VIIIb**, **VIIIf–VIIh**, **VIIIp**, **trans-VIIe**, and **trans-VIIg** and mixtures **VIIIi/cis-VIIIf**, **VIIIk/cis-VIIg**, **VIIIi/cis-VIIh** and **VIIIo/cis-VIIIi**, on a Bruker DRX-500 instrument (500 MHz) from solutions in DMSO-*d*<sub>6</sub>; tetramethylsilane was used as internal reference. The  $^1\text{H}$  NMR spectra of **VIIIj** and **VIIIIn** were measured on an RYa-2310 spectrometer (60 MHz) from solutions in DMSO-*d*<sub>6</sub>–CDCl<sub>3</sub> using hexamethyldisiloxane as internal reference. The  $^{13}\text{C}$  NMR spectra of **VIIIe**, **VIIIm**, and **trans-VIIb** were obtained on a Bruker DRX-400 spectrometer at 100.6 MHz from solutions in DMSO-*d*<sub>6</sub>.

**N-Cyclohexyl- and *N*-aryl-1-aryl-1-alkyl-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamides *cis*-VIIa–*cis*-VIIe and *cis*-VIIIf–*cis*-VIIIi (general procedure).** 1-Aryl-2,2-dibromoalkanone **Ia–Ih**, 0.03 mol, was added to a mixture of 4 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 15 min under reflux and cooled, and the liquid phase was separated by decanting and transferred into another flask. Compound **III**, 0.01 mol, was added, and the mixture was heated for 30–40 min under reflux, cooled, treated with acetic acid, and extracted with appropriate solvent. The extract was evaporated, and the residue was recrystallized from acetone or methanol.

**N-Cyclohexyl-, *N*-aryl-, and *N*-benzyl-1-aryl-1-alkyl-(6-bromo)-2-oxo-1a,7b-dihydro-cyclopropa[c]chromene-1a-carboxamides *trans*-VIIa–*trans*-VIIh** were synthesized in a similar way with the

difference that 2 ml of HMPA was added in the second step.

**1-Aryl-2-benzyl-, 1-aryl-2-benzyl-8-bromo-, and 1,2-diaryl-9c-alkyl-1-hydroxy-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropano[1,2-a]naphthalene-3,4-diones VIIa–VIIp** were synthesized as described above for *cis*-VIIa–*cis*-VIIi.

**N-Cyclohexyl-1-(4-fluorobenzoyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*cis*-VIIa).** Yield 58%, mp 197–198°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1675, 1730, 3370.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.00–1.65 m (10H,  $\text{C}_6\text{H}_{11}$ ), 1.13 s (3H, Me), 3.31 m (1H,  $\text{C}_6\text{H}_{11}$ ), 3.75 s (1H, CH), 7.18–7.91 m (8H,  $\text{C}_6\text{H}_4$ , 4-FC $\text{C}_6\text{H}_4$ ), 8.23 m (1H, NH). Found, %: C 71.16; H 5.63.  $\text{C}_{25}\text{H}_{24}\text{FNO}_4$ . Calculated, %: C 71.25; H 5.74.

**1-(4-Chlorobenzoyl)-N-cyclohexyl-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*cis*-VIIb).** Yield 63%, mp 184–185°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1675, 1730, 3370.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.00–1.80 m (10H,  $\text{C}_6\text{H}_{11}$ ), 1.12 s (3H,  $\text{CH}_3$ ), 3.31 m (1H,  $\text{C}_6\text{H}_{11}$ ), 3.75 s (1H, CH), 7.17–7.84 m (8H,  $\text{C}_6\text{H}_4$ , 4-ClC $\text{C}_6\text{H}_4$ ), 8.24 d (1H, NH). Found, %: C 68.58; H 5.59.  $\text{C}_{25}\text{H}_{24}\text{ClNO}_4$ . Calculated, %: C 68.57; H 5.52.

**1-(4-Bromobenzoyl)-N-cyclohexyl-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*cis*-VIIc).** Yield 53%, mp 186–188°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1670, 1730, 3370.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.00–1.80 m (10H,  $\text{C}_6\text{H}_{11}$ ), 1.12 s (3H, Me), 3.32 m (1H,  $\text{C}_6\text{H}_{11}$ ), 3.75 s (1H, CH), 6.82–7.76 m (8H,  $\text{C}_6\text{H}_4$ , 4-BrC $\text{C}_6\text{H}_4$ ), 8.26 d (1H, NH).

$^1\text{H}$  NMR spectrum of the minor isomer,  $\delta$ , ppm: 1.57 s (3H, Me), 3.67 m (1H,  $\text{C}_6\text{H}_{11}$ ), 3.60 s (1H, CH), 8.35 d (1H, NH). Found, %: C 62.15; H 4.95.  $\text{C}_{25}\text{H}_{24}\text{BrNO}_4$ . Calculated, %: C 62.25; H 5.02.

**1-Benzoyl-N-cyclohexyl-1-ethyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*cis*-VIId).** Yield 46%, mp 166–167°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1675, 1730, 3370.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.46 t (3H, Me), 0.98–1.63 m (10H,  $\text{C}_6\text{H}_{11}$ ), 1.16 m (1H,  $\text{CH}_2$ ), 1.96 m (1H,  $\text{CH}_2$ ), 3.30 m (1H,  $\text{C}_6\text{H}_{11}$ ), 3.74 s (1H, CH), 6.83–8.40 m (10H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , NH). Found, %: C 74.71; H 6.56.  $\text{C}_{26}\text{H}_{27}\text{NO}_4$ . Calculated, %: C 74.80; H 6.52.

**1-(4-Chlorobenzoyl)-N-cyclohexyl-1-ethyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*cis*-VIIe).** Yield 56%, mp 191–192°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1680, 1730, 3370.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.45 t (3H, Me), 1.00–1.60 m (10H,

$\text{C}_6\text{H}_{11}$  and 1H,  $\text{CH}_2$ ), 1.95 m (1H,  $\text{CH}_2$ ), 3.30 m (1H,  $\text{C}_6\text{H}_{11}$ ), 3.70 s (1H, CH), 7.17–7.88 m (8H,  $\text{C}_6\text{H}_4$ , 4-ClC $\text{C}_6\text{H}_4$ ), 8.24 d (1H, NH). Found, %: C 68.95; H 5.85.  $\text{C}_{26}\text{H}_{26}\text{ClNO}_4$ . Calculated, %: C 69.10; H 5.80.

**1-(4-Chlorobenzoyl)-N-cyclohexyl-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*trans*-VIIa).** Yield 35%, mp 234–235°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1725, 3360.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.57 s (3H, Me), 3.59 s (1H, CH), 3.64 m (1H,  $\text{C}_6\text{H}_{11}$ ), 6.83–7.88 m (8H,  $\text{C}_6\text{H}_4$ , 4-ClC $\text{C}_6\text{H}_4$ ), 8.44 s (1H, NH). Found, %: C 68.46; H 5.65.  $\text{C}_{25}\text{H}_{24}\text{ClNO}_4$ . Calculated, %: C 68.57; H 5.52.

**1-Benzoyl-N-benzyl-6-bromo-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*trans*-VIIb).** Yield 40%, mp 199–200°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1725, 3360.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.60 s (3H, Me), 3.68 s (1H, CH), 4.39 d.d and 4.46 d.d (2H,  $\text{NCH}_2$ ,  $J$  = 15.1, 6.0 Hz), 6.83 d (1H, 4-H,  $J$  = 8.7 Hz), 7.23–7.36 m (5H,  $\text{CH}_2\text{C}_6\text{H}_5$ ), 7.28 d.d (1H, 5-H,  $J$  = 8.7, 2.5 Hz), 7.47 d.d (2H, 3'-H, 5'-H,  $J$  = 8.3, 7.4 Hz), 7.60 t.t (1H, 4'-H,  $J$  = 7.4, 1.2 Hz), 7.90 d.d (2H, 2'-H, 6'-H,  $J$  = 8.3, 1.2 Hz), 8.00 d (1H, 7-H,  $J$  = 2.5 Hz), 9.16 br.t (1H, NH,  $J$  = 6.0 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 19.38 ( $\text{CH}_3$ ), 34.79 ( $\text{C}^{\text{7b}}$ ), 38.44 ( $\text{C}^{\text{1a}}$ ), 42.93 ( $\text{NCH}_2$ ), 43.46 ( $\text{C}^{\text{1}}$ ), 115.73 ( $\text{C}^{\text{6}}$ ), 118.04 ( $\text{C}^{\text{4}}$ ), 120.53 ( $\text{C}^{\text{7a}}$ ), 126.83 ( $\text{C}^{\text{p}}$ ), 127.29 ( $\text{C}^{\text{o}}$ ), 128.22 ( $\text{C}^{\text{m}}$ ), 128.63 ( $\text{C}^{\text{3}}$ ,  $\text{C}^{\text{5}}$ ), 129.29 ( $\text{C}^{\text{2}}$ ,  $\text{C}^{\text{6}}$ ), 131.07 ( $\text{C}^{\text{5}}$ ), 131.96 ( $\text{C}^{\text{7}}$ ), 132.89 ( $\text{C}^{\text{l}}$ ), 133.90 ( $\text{C}^{\text{4}}$ ), 138.89 ( $\text{C}^{\text{i}}$ ), 147.86 ( $\text{C}^{\text{3a}}$ ), 162.95 ( $\text{C}^{\text{2}}$ ), 163.00 (NC=O), 194.23 (C=O). Found, %: C 63.58; H 4.03.  $\text{C}_{26}\text{H}_{20}\text{BrNO}_4$ . Calculated, %: C 63.69; H 4.11.

**N-Benzyl-6-bromo-1-(4-chlorobenzoyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*trans*-VIIc).** Yield 48%, mp 246–247°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1725, 3360.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.58 s (3H, Me), 3.65 s (1H, CH), 4.38 m and 4.44 m (2H,  $\text{CH}_2$ ), 6.82–7.92 m (12H,  $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_5$ , 4-ClC $\text{C}_6\text{H}_4$ ), 9.14 m (1H, NH). Found, %: C 59.58; H 3.72.  $\text{C}_{26}\text{H}_{19}\text{BrClNO}_4$ . Calculated, %: C 59.51; H 3.65.

**N-Benzyl-6-bromo-1-(4-bromobenzoyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropano[c]chromene-1a-carboxamide (*trans*-VIId).** Yield 25%, mp 257–259°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1725, 3360.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.59 s (3H, Me), 3.65 s (1H, CH), 4.43 m and 4.52 m (2H,  $\text{CH}_2$ ), 6.48–7.88 m (12H,  $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_5$ , 4-BrC $\text{C}_6\text{H}_4$ ), 9.00 m (1H, NH). Found, %: C 54.81; H 3.44.  $\text{C}_{26}\text{H}_{19}\text{Br}_2\text{NO}_4$ . Calculated, %: C 54.86; H 3.36.

**1-(4-Chlorobenzoyl)-1-methyl-2-oxo-N-phenyl-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*trans*-VIIe).** Yield 43%, mp 254–255°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1675, 1725, 3330.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.69 s (3H, Me), 3.72 s (1H, CH), 6.90–7.90 m (13H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , 4-Cl $\text{C}_6\text{H}_4$ ), 10.53 s (1H, NH). Found, %: C 69.65; H 4.12.  $\text{C}_{25}\text{H}_{16}\text{ClNO}_4$ . Calculated, %: C 69.53; H 4.20.

**1-Benzoyl-1-methyl-N-(4-methylphenyl)-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*trans*-VIIf).** Yield 35%, mp 223–225°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1675, 1725, 3315.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.70 s (3H, Me), 2.32 s (3H,  $\text{CH}_3$ ), 3.70 s (1H, CH), 6.81–7.83 m (13H,  $\text{C}_6\text{H}_4$ , 4-Me $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ ), 10.35 s (1H, NH). Found, %: C 75.79; H 5.21.  $\text{C}_{26}\text{H}_{21}\text{NO}_4$ . Calculated, %: C 75.90; H 5.14.

**1-(4-Fluorobenzoyl)-1-methyl-N-(4-methylphenyl)-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*trans*-VIIg).** Yield 36%, mp 241–242°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1675, 1730, 3315.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.69 s (3H, Me), 2.27 s (3H,  $\text{CH}_3$ ), 3.71 s (1H, CH), 6.88–7.98 m (12H,  $\text{C}_6\text{H}_4$ , 4-Me $\text{C}_6\text{H}_4$ , 4-FC $\text{C}_6\text{H}_4$ ), 10.42 s (1H, NH). Found, %: C 72.86; H 4.63.  $\text{C}_{26}\text{H}_{20}\text{FNO}_4$ . Calculated, %: C 72.72; H 4.69.

**1-(4-Chlorobenzoyl)-1-ethyl-N-(4-methylphenyl)-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*trans*-VIIh).** Yield 40%, mp 220–221°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1680, 1730, 3320.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.88 t (3H, Me), 2.08 m and 2.25 m (2H,  $\text{CH}_2$ ), 2.34 s (3H,  $\text{CH}_3$ ), 3.80 s (1H, CH), 6.81–7.92 m (12H,  $\text{C}_6\text{H}_4$ , 4-Me $\text{C}_6\text{H}_4$ , 4-Cl $\text{C}_6\text{H}_4$ ), 10.50 s (1H, NH). Found, %: C 70.66; H 4.72.  $\text{C}_{27}\text{H}_{22}\text{ClNO}_4$ . Calculated, %: C 70.51; H 4.82.

**2-Benzyl-1-(4-chlorophenyl)-1-hydroxy-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]-cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIa).** Yield 56%, mp 228–229°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1665, 1750, 3200.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.51 s (3H,  $\text{CH}_3$ ), 3.60 s (1H, CH), 3.80 d, 4.27 d (2H,  $\text{CH}_2$ ), 6.92–7.78 m (14H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , 4-Cl $\text{C}_6\text{H}_4$ , OH). Found, %: C 69.90; H 4.43.  $\text{C}_{26}\text{H}_{20}\text{ClNO}_4$ . Calculated, %: C 70.03; H 4.52.

**2-Benzyl-1-(4-bromophenyl)-1-hydroxy-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]-cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIb).** Yield 47%, mp 248–250°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1660, 1750, 3250.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.52 s (3H,  $\text{CH}_3$ ), 3.60 s (1H, CH), 3.80 d and 4.28 d (2H,  $\text{CH}_2$ ), 6.86–7.70 m (14H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , 4-Br $\text{C}_6\text{H}_4$ ,

OH). Found, %: C 63.75; H 4.19.  $\text{C}_{26}\text{H}_{20}\text{BrNO}_4$ . Calculated, %: C 63.69; H 4.11.

**2-Benzyl-8-bromo-1-(4-chlorophenyl)-1-hydroxy-9c-methyl-1,2,9b,9s-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIc).** Yield 50%, mp 221–223°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1665, 1760, 3320.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.61 s (3H, Me), 3.50 s (1H, CH), 3.75 d and 4.33 d (2H,  $\text{CH}_2$ ,  $J$  = 15.5 Hz), 6.86–7.8 m (13H,  $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_5$ , 4-Cl $\text{C}_6\text{H}_4$ , OH). Found, %: C 59.42; H 3.60.  $\text{C}_{26}\text{H}_{19}\text{BrClNO}_4$ . Calculated, %: C 59.51; H 3.65.

**2-Benzyl-8-bromo-1-(4-chlorophenyl)-9c-ethyl-1-hydroxy-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIId).** Yield 45%, mp 222–223°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1665, 1760, 3300.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.60 s (3H,  $\text{CH}_3$ ), 0.77 m and 1.17 m (2H,  $\text{CH}_2$ ), 3.51 s (1H, CH), 3.70 d and 4.27 d (2H,  $\text{CH}_2$ ), 6.90–7.90 m (13H,  $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_5$ , 4-Cl $\text{C}_6\text{H}_4$ , OH). Found, %: C 60.28; H 3.85.  $\text{C}_{26}\text{H}_{19}\text{BrClNO}_4$ . Calculated, %: C 60.19; H 3.93.

**2-Benzyl-8-bromo-1-(4-bromophenyl)-9c-ethyl-1-hydroxy-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIf).** Yield 50%, mp 207–208°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1665, 1760, 3300.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.54 t (3H,  $\text{CH}_3$ ,  $J$  = 7.3 Hz), 0.71 d.q and 1.09 d.q (2H,  $\text{CH}_2$ ,  $J$  = 14.6, 7.3 Hz), 3.60 s (1H, 9b-H), 3.72 d and 4.26 d (2H,  $\text{NCH}_2$ ,  $J$  = 15.5 Hz), 6.89 d.d (1H, 6'-H,  $J$  = 8.4, 2.4 Hz), 7.10 d (1H, 6-H,  $J$  = 8.8 Hz), 7.16–7.27 m (5H,  $\text{CH}_2\text{C}_6\text{H}_5$ ), 7.23 s (1H, OH), 7.55 d.d (1H, 7-H,  $J$  = 8.8, 2.5 Hz), 7.62 d.d (1H, 5'-H,  $J$  = 8.4, 2.0 Hz), 7.67 d.d (1H, 3'-H,  $J$  = 8.4, 2.0 Hz), 7.80 d.d (1H, 2'-H,  $J$  = 8.4, 2.4 Hz), 7.92 d (1H, 9-H,  $J$  = 2.5 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 9.74 (Me), 17.76 ( $\text{CH}_2$ ), 33.22 ( $\text{C}^{9b}$ ), 36.76 ( $\text{C}^{3a}$ ), 41.55 ( $\text{C}^{9c}$ ), 42.66 ( $\text{NCH}_2$ ), 92.06 ( $\text{C}^1$ ), 116.31 ( $\text{C}^8$ ), 118.74 ( $\text{C}^6$ ), 118.99 ( $\text{C}^{9a}$ ), 122.10 ( $\text{C}^4$ ), 126.70 ( $\text{C}^p$ ), 127.51 ( $\text{C}^o$ ), 127.59 ( $\text{C}^6$ ), 128.01 ( $\text{C}^m$ ), 129.38 ( $\text{C}^2$ ), 131.43 ( $\text{C}^3$ ), 131.67 ( $\text{C}^5$ ), 131.67 ( $\text{C}^9$ ), 131.94 ( $\text{C}^7$ ), 137.60 ( $\text{C}^i$ ), 139.09 ( $\text{C}^1$ ), 149.20 ( $\text{C}^{5a}$ ), 159.28 ( $\text{C}^4$ ), 165.87 ( $\text{C}^3$ ). Found, %: C 55.47; H 3.54.  $\text{C}_{27}\text{H}_{21}\text{Br}_2\text{NO}_4$ . Calculated, %: C 55.60; H 3.63.

**9c-Ethyl-1-hydroxy-1,2-diphenyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIf).** Yield 31%, mp 228–229°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690, 1735, 3470.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.54 t (3H,  $\text{CH}_3$ ), 0.77 m, 1.16 m (2H,  $\text{CH}_2\text{CH}_3$ ), 3.89 s (1H, CH), 7.00–7.74 m (15H,  $\text{C}_6\text{H}_4$ , 2 $\text{C}_6\text{H}_5$ , OH). Found, %: C 75.86; H 5.21.  $\text{C}_{26}\text{H}_{21}\text{NO}_4$ . Calculated, %: C 75.90; H 5.14.

**1-(4-Chlorophenyl)-9c-ethyl-1-hydroxy-2-phenyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIg).** Yield 48%, mp 242–243°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1700, 1760, 3390.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.55 t (3H,  $\text{CH}_3$ ), 0.80 m, 1.38 m (2H,  $\text{CH}_2\text{CH}_3$ ), 3.89 s (1H, CH), 7.02–7.74 m (14H,  $\text{C}_6\text{H}_4$ ,  $\text{C}_6\text{H}_5$ , 4-Cl $\text{C}_6\text{H}_4$ , OH). Found, %: C 70.13; H 4.45.  $\text{C}_{26}\text{H}_{20}\text{ClNO}_4$ . Calculated, %: C 70.03; H 4.52.

**9c-Ethyl-1-hydroxy-1,2-bis(4-methylphenyl)-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]-cyclopropa[1,2-a]naphthalen-3,4-dione (VIIIh).** Yield 43%, mp 244–245°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1700, 1745, 3480.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.55 s (3H, Me), 2.22 s (3H, Me), 2.31 s (3H, Me), 3.81 s (1H, CH), 6.90–7.60 m (13H,  $\text{C}_6\text{H}_4$ , 4-Me $\text{C}_6\text{H}_4$ , OH). Found, %: C 76.29; H 5.33.  $\text{C}_{27}\text{H}_{23}\text{NO}_4$ . Calculated, %: C 76.22; H 5.45.

**1-(4-Chlorophenyl)-1-hydroxy-9c-methyl-2-(4-methylphenyl)-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIi) and 1-(4-chlorobenzoyl)-1-methyl-N-(4-methylphenyl)-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*cis*-VIIIf) (55:45 isomer mixture).** Yield 69%, mp 227–228°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690, 1755, 3460.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.57 s (3H, Me), 2.21 s (3H, Me), 3.76 s (1H, CH), 6.93–7.50 m (13H,  $\text{C}_6\text{H}_4$ , 4-Me $\text{C}_6\text{H}_4$ , 4-Cl $\text{C}_6\text{H}_4$ , OH), 1.02 s (3H, Me), 2.22 s (3H, Me), 3.74 s (1H, CH), 7.85 s (1H, NH). Found, %: C 69.91; H 4.40.  $\text{C}_{26}\text{H}_{20}\text{ClNO}_4$ . Calculated, %: C 70.03; H 4.52.

**2-(4-Bromophenyl)-1-(4-fluorophenyl)-1-hydroxy-9c-methyl-1,2,9b,9s-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIj).** Yield 32%, mp 226–227°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690, 1740, 3450.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.6 s (3H, Me), 3.8 s (1H, CH), 6.8–7.8 m (13H,  $\text{C}_6\text{H}_4$ , 4-Br $\text{C}_6\text{H}_4$ , 4-FC $\text{C}_6\text{H}_4$ , OH). Found, %: C 60.61; H 3.55.  $\text{C}_{25}\text{H}_{17}\text{BrFNO}_4$ . Calculated, %: C 60.75; H 3.47.

**2-(4-Bromophenyl)-1-(4-chlorophenyl)-9c-ethyl-1-hydroxy-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIk) and N-(4-bromophenyl)-1-(4-chlorobenzoyl)-1-ethyl-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*cis*-VIIg) (58:42 isomer mixture).** Yield 50%, mp 228–229°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1690, 1755, 3460.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.55 t (3H, Me), 0.80 m (1H,  $\text{CH}_2$ ), 1.15 m (1H,  $\text{CH}_2$ ), 3.90 s (1H, CH), 7.00–7.70 m (13H,  $\text{C}_6\text{H}_4$ , 4-Br $\text{C}_6\text{H}_4$ , 4-Cl $\text{C}_6\text{H}_4$ , OH), 0.44 t (3H, Me), 1.13 m (1H,  $\text{CH}_2$ ),

2.14 m (1H,  $\text{CH}_2$ ), 4.01 s (1H, CH), 8.02 s (1H, NH). Found, %: C 59.63; H 3.58.  $\text{C}_{26}\text{H}_{19}\text{BrClNO}_4$ . Calculated, %: C 59.51; H 3.65.

**1-(4-Chlorophenyl)-1-hydroxy-2-(4-methoxyphenyl)-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIi) and 1-(4-chlorobenzoyl)-N-(4-methoxyphenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxamide (*cis*-VIIh) (84:16 isomer mixture).** Yield 67%, mp 237–238°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1700, 1740, 3490.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.56 s (3H, Me), 3.63 s (3H, Me), 3.73 s (1H, CH), 6.85–7.60 m (13H,  $\text{C}_6\text{H}_4$ , 4-MeOC $\text{C}_6\text{H}_4$ , 4-Cl $\text{C}_6\text{H}_4$ , OH), 1.03 s (3H, Me), 3.63 s (3H, OMe), 3.75 s (1H, CH), 7.84 s (1H, NH). Found, %: C 67.78; H 4.42.  $\text{C}_{26}\text{H}_{20}\text{ClNO}_5$ . Calculated, %: C 67.61; H 4.36.

**1-(4-Bromophenyl)-1-hydroxy-2-(4-methoxyphenyl)-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIIm).** Yield 53%, mp 239–241°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1710, 1750, 3490.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.58 s (3H, Me); 3.70 s (3H, OMe); 3.88 s (1H, 9b-H); 6.85 d (2H, *m*-H,  $J$  = 9.0 Hz); 6.96 d (2H, *o*-H,  $J$  = 9.0 Hz); 7.14 d.d (1H, 6-H,  $J$  = 8.0, 1.1 Hz); 7.30 t.d (1H, 8-H,  $J$  = 7.5, 1.1 Hz); 7.40 d.d.d (1H, 7-H,  $J$  = 8.0, 7.5, 1.7 Hz); 7.40 s (1H, OH); 7.62 d.d (1H, 9-H,  $J$  = 7.5, 1.7 Hz); 7.27 br.s, 7.50 br.s, 7.58 br.s, and 7.75 br.s (1H each, 2'-H, 3'-H, 5'-H, 6'-H). Found, %: C 61.52; H 3.89.  $\text{C}_{26}\text{H}_{20}\text{BrNO}_5$ . Calculated, %: C 61.67; H 3.98.

**1-Hydroxy-2-(2-methoxyphenyl)-9c-methyl-1-(4-methylphenyl)-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIIn).** Yield 40%, mp 249–250°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1700, 1745, 3490.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.57 s (3H, Me), 2.3 s (3H, Me), 3.7 s (3H, Me, and 1H, CH), 6.7–7.5 m (13H,  $\text{C}_6\text{H}_4$ , 4-MeOC $\text{C}_6\text{H}_4$ , 4-Me $\text{C}_6\text{H}_4$ , OH). Found, %: C 73.34; H 5.29.  $\text{C}_{27}\text{H}_{23}\text{NO}_5$ . Calculated, %: C 73.46; H 5.25.

**1-(4-Chlorophenyl)-1-hydroxy-2-(2-methoxyphenyl)-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-a]naphthalene-3,4-dione (VIIIo) and 1-(4-chlorobenzoyl)-N-(2-methoxyphenyl)-1-methyl-2-oxo-1a,7b-dihydrocyclopropa[c]chromene-1a-carboxylate (*cis*-VIIIi) (57:43 isomer mixture).** Yield 42%, mp 265–267°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1700, 1740, 3480.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.58 s (3H, Me), 3.39 s (1H, CH), 3.79 s (3H, OMe), 6.75–7.80 m (13H,  $\text{C}_6\text{H}_4$ ,

4-MeOC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, OH), 1.03 s (3H, Me), 3.70 s (3H, OMe), 3.91 s (1H, CH). Found, %: C 67.50; H 4.42. C<sub>26</sub>H<sub>20</sub>ClNO<sub>5</sub>. Calculated, %: C 67.61; H 4.36.

**1-(4-Bromophenyl)-1-hydroxy-2-(2-methoxyphenyl)-9c-methyl-1,2,9b,9c-tetrahydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-3,4-dione (VIIp).** Yield 48%, mp 264–265°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1700, 1720–1750, 3490. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.59 s (3H, Me), 3.70 s (3H, Me), 3.79 s (1H, CH), 6.50–7.73 m (13H, C<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, OH). Found, %: C 61.49; H 3.91. C<sub>26</sub>H<sub>20</sub>BrNO<sub>5</sub>. Calculated, %: C 61.67; H 3.98.

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