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Reaction of N-Substituted 2-Oxochromen-3-carboxamides with Bromoderivatives of Zinc Enolates Prepared from Alkyl 2,2-Dialkyl-4,4-dibromo-3-oxoalkanoates and Zinc

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Abstract—Zinc enolates obtained from ethyl 2,2-dialkyl-4,4-dibromo-3-oxobutanoates and zinc react with N-substituted 2-oxochromen-3-carboxamides forming ethyl 3-{1a-(R^3-carbamoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-dialkyl-3-oxopropanoate isomer with a *Z*-position of methine hydrogens. Zinc enolates prepared from alkyl 2,2-dialkyl-4,4-dibromo-3-oxopentanoates and –hexanoates and zinc react with N-substituted 2-oxochromen-3-carboxamides to give rise to esters of 3-{1-alkyl-1a-(R^3-carbamoyl)-2-oxo-1a,7b-dihydrocyclopropa-[*c*]chromen-1-yl}-2,2-dialkyl-3-oxopropanoic acid as isomers with the *E*-position of the methine proton and the alkyl substituent. The reaction carried out in the presence of small quantities of THF and HMPA leads to the formation of 9c-alkyl-2-R^3-9b,9c-dihydro-5-oxa-2-azacyclopenta[2,3]-cyclopropa[1,2-*a*]naphthalene-1,3,4-triones. Zinc enolates from alkyl 2,2-dialkyl-4,4-dibromo-3-oxopentanoates and –hexanoates and zinc with the secondary amides of 2-oxochromen-3-carboxylic acid form alkyl 3-{2-oxo-1a-(piperidinocarbonyl)- and 3-{6-R^1-1a-(morpholinocarbonyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-R^2,R^2-3-oxopropanoates as single geometrical isomers.

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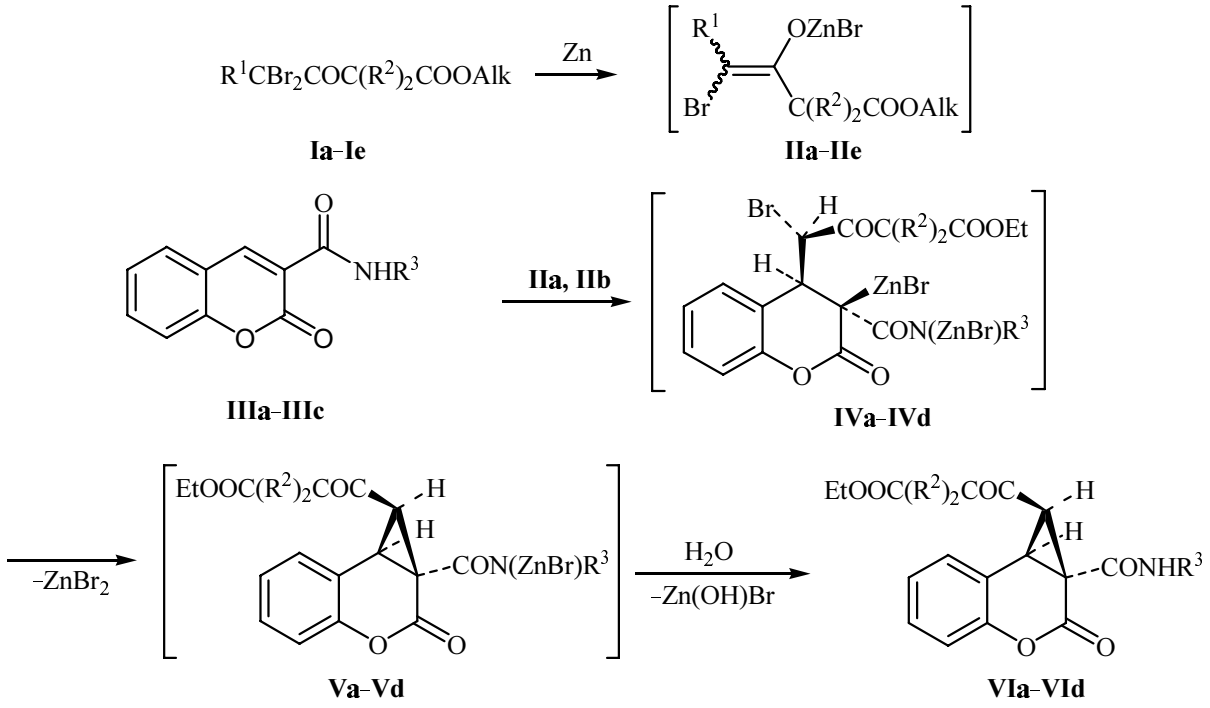
We showed formerly that 2-oxochromen-3-carboxylic acid derivatives underwent cyclopropanation at the treatment with zinc enolates bromoderivatives prepared from 1-aryl-2,2-dibromoalkanones and zinc leading to the formation of cyclopropane derivatives containing an aroyl group as a functional substituent in the ring [1].

In the present study we attempted to prepare cyclopropane derivatives containing instead of the aroyl group a fragment with two functional group, namely, 2,2-dialkyl-1,3-dioxo-3-alkoxypropyl moiety. To this end we investigated the reaction of zinc enolates **IIa** and **IIb** obtained from ethyl 2,2-dialkyl-4,4-dibromo-3-oxanoates **Ia** and **Ib** with N-substituted 2-oxochromen-3-carboxamides **IIIa** and **IIIb**. The experiments demonstrated that the reaction proceeded along Scheme 1.

First one molecule of zinc enolate takes off the "acidic" hydrogen from amide groups of electrophilic substrates **IIIa–IIIc**, then the second enolate molecule adds regiospecifically to the double bond of the heterocycle giving intermediates **IVa–IVd**. The latter undergo a stereospecific cyclization into compounds **Va–Vd** that are hydrolyzed into ethyl 3-{1a-(R^3-carbamoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-R^2,R^2-3-oxopropanoates **VIa–VId**.

The composition and structure of compounds **VIa–VId** were proved by elemental analysis, IR and ^{1}H NMR spectroscopy. The IR spectra contain characteristic absorption bands of amide group carbonyl at 1670–1685 cm^{-1}, carbonyls of keto, lactone, and ester groups in the region 1715–1760, and of N–H bonds in the region 3325–3380 cm^{-1}. In the ^{1}H NMR spectrum of, e.g, ethyl 3-{1a-(4-methylphenylcarbamoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-dimethyl-3-oxopropanoate (**VIa**) characteristic proton signals appear at δ, ppm: 1.05–1.25 m (3Me), 3.21 d, 3.77 d (2CH, ^3J 9.7 Hz), 4.05 q (CH_2). The spectral data suggest that compound **VIa** formed as a single diastereomer. The spin–spin coupling constants of the vicinal hydrogens attached to a cyclopropane ring in analogous chromen derivatives are known from the published data to be quite dissimilar (J_{cis} 9.4–9.8, J_{trans} 5.1–5.5 Hz) [2]. The value ^3J 9.7 Hz in compound **VIa** unambiguously proves the *cis*-location of the hydrogen atoms with respect to the plane of the cyclopropane ring. Based on the ^3J values a conclusion

Scheme 1.



I, II, R^1 = H, Alk = Et, R^2 = Me (**a**), Et (**b**); R^1 = Et, R^2 = Me, Alk = Me (**c**), Et (**d**); R^1 = Alk = R^2 = Me (**e**); **III**, R^3 = 4-MeC_6H_4 (**a**), CH_2Ph (**b**), C_6H_{11} (**c**); **IV–VI**, R^2 = Me, R^3 = 4-MeC_6H_4 (**a**); R^2 = Et, R^3 = CH_2Ph (**b**), 4-MeC_6H_4 (**c**), C_6H_{11} (**d**).

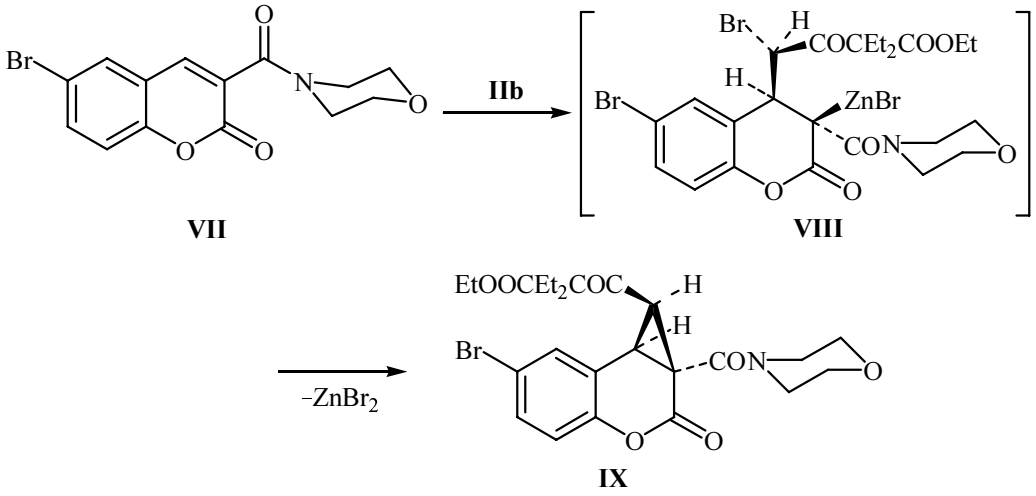
follows that likewise all compounds of this series **VIb–VId** have a similar structure.

Morpholide **VII** lacking a labile hydrogen atom at the nitrogen easily reacted in a similar way with zinc enolate **IIb** and via intermediate **VIII** formed ethyl 3-{6-bromo-1a-(4-morpholinocarbonyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-diethyl-3-oxopropanoate (**IX**) (Scheme 2).

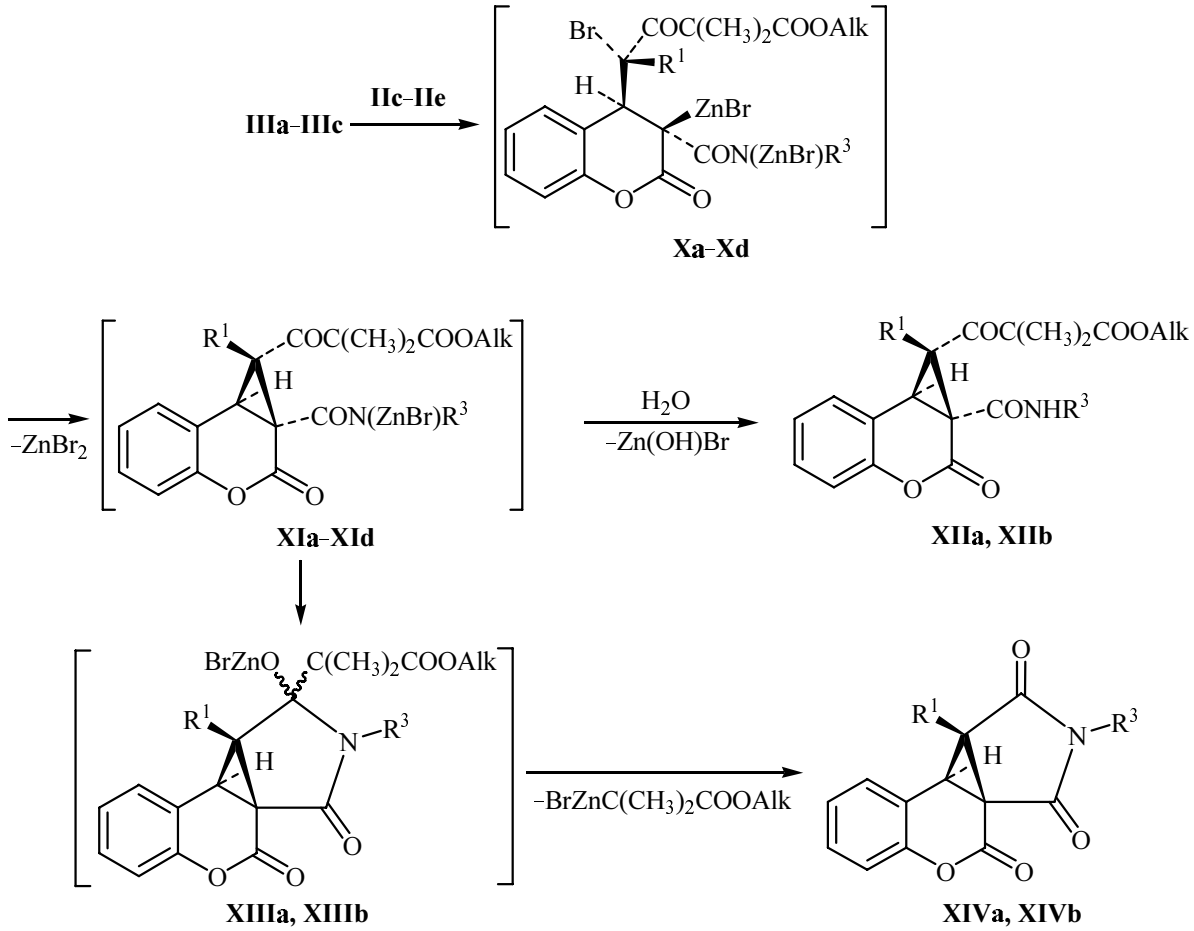
It should be noted that the reference constant ^3J value in compound **IX** equals 7.4 Hz, somewhat smaller, than in analogous compounds **VIa–VId**. Nonetheless the reactions under consideration presumably proceed with analogous stereochemistry, and the stereo configurations of compounds **VIa–VId** and **IX** are similar.

We further carried out the reaction of zinc enolates **IId** and **IIe** possessing at the C-nucleophilic site an alkyl

Scheme 2.



Scheme 3.



X, XI, R^1 = Et, R^3 = C_6H_{11}, Alk = Me (**a**), Et (**b**); R^1 = Alk = Me, R^3 = CH_2Ph (**c**), 4-MeC_6H_4 (**d**); **XII**, R^1 = Et, R^3 = C_6H_{11}, Alk = Me (**a**), Et (**b**); **XIII**, R^1 = Alk = Me, R^3 = CH_2Ph (**a**), 4-MeC_6H_4 (**b**); **XIV**, R^1 = Me, R^3 = CH_2Ph (**a**), 4-MeC_6H_4 (**b**).

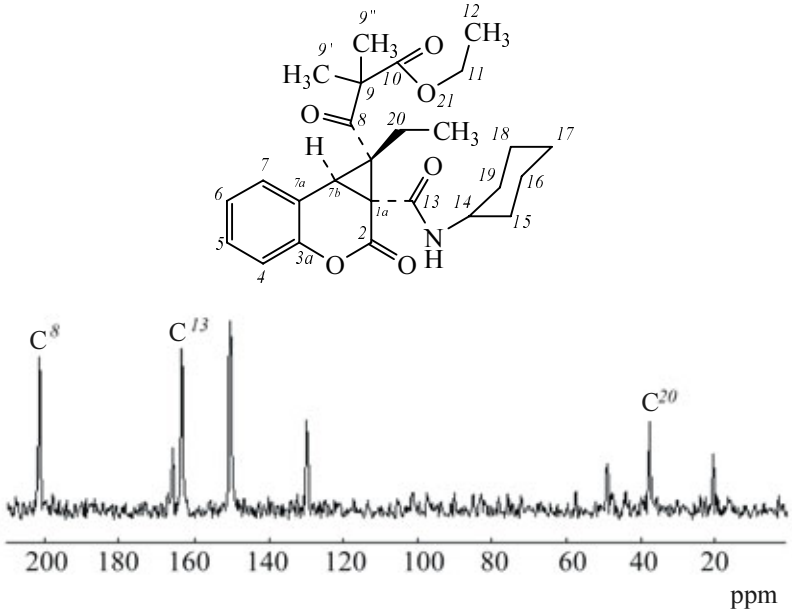
group R^2 with primary 2-oxochromen-3-carboxamides **IIIa–IIIc**. In the first stage the reaction takes a similar route and proceeds through intermediates **Xa** and **Xb**, **XIa** and **XIb** leading to the formation of alkyl 3-{1-alkyl-1a-(R^3-carbamoyl)-2-oxo-1a,7b-dihydrocyclopropa-[*c*]chromen-1-yl}-2,2-dimethyl-3-oxopropanoates **XIIa** and **XIIb** (Scheme 3).

In the IR spectra of compound **XIIa** and **XIIb** appear the absorption bands of amide group carbonyl at 1650 cm^{-1}, carbonyls of keto, lactone, and ester groups in the region 1720–1740, and of N–H bond in the region 3360 cm^{-1}. The ^1H NMR spectrum contains one characteristic signal of methine proton at 3.83–3.87 ppm, indicating that compounds **XIIa** and **XIIb** form as single diastereomers.

To confirm the structure of compounds **XIIa** and **XIIb** obtained and to reveal the relative position of the substituents at the cyclopropane ring we investigated compound **XIIb** by means of ^{13}C NMR spectroscopy, including registering the spectra without protons decoupling to estimate $^nJ_{CH}$ coupling constants, and also applying 2D-methods (HSQC, HMBC, and NOESY).

In estimating the stereo configuration of the cyclopropane fragment the vicinal coupling constants $^3J_{CH}$ of the H^{7b} proton with atoms C^{8}, C^{13}, and C^{20} are the most informative. However in the ^{13}C NMR spectrum registered without decoupling from protons the signals of these atoms appear as a rule in the form of complex unresolved multiplets unfit for an unambiguous evaluation of the constants in question. The selective decoupling mode also failed to help in the analysis of the multiplets.

An approximate estimation of $^3J_{CH}$ value may be done using the known relation of the intensity of the cross-peaks in the 2D HMBC spectrum to the value of the constant generating this cross-peak [3]. From the section of the HMBC spectrum along the F1 axis going through



Cross-section of the 2D ^{1}H–^{13}C HMBC spectrum of compound **XIIb** along the F1 axis through the signal of H^{7b} proton.

the signal of H^{7b} (see the figure) the ratio of the constants may be estimated at $^{3}J_{C^{8},H^{7b}} \approx {}^{3}J_{C^{13},H^{7b}} > {}^{3}J_{C^{20},H^{7b}}$.

Thus the comparison between the vicinal constants $^{3}J_{C^{8},H^{7b}}$, $^{3}J_{C^{13},H^{7b}}$, and $^{3}J_{C^{20},H^{7b}}$, and also with the previously measured values of analogous constants in the spectra of similar compounds permits an assumption that in the structure of compound **XIIb** the H^{7b} proton is situated in the *cis*-position with respect to the carbonyl atoms C^{8} and C^{13} and in the *trans*-position relative to the atom C^{20}. This conclusion is supported also by the analysis of NOE observed in the spectra 2D NOESY: The H^{7b} proton has a strong cross-peak with the H^{7} proton, more weak cross-peaks with the methyl protons $H^{9'}$ and $H^{9''}$, and a very weak cross-peak with one of the nonequivalent methylene protons H^{20B}. This result indicates that the 2,2-dialkyl-1,3-dioxo-3-alkoxypropyl substituent and the amide group are located on the same side with respect to the cyclopropane ring plane.

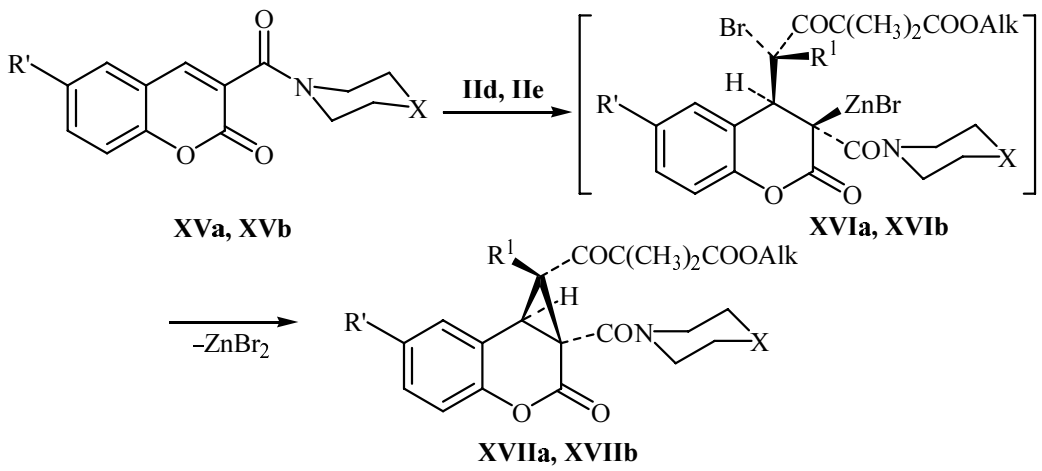
To confirm the stereo configuration of compounds **XIIa** and **XIIb** we investigated the reaction of zinc enolate **IIc** with amides **IIIb** and **IIIc** in a mixture ether–ethyl acetate adding small amounts of THF and HMPA. The presence of the additives drastically changes the outcome of the chemical reaction. As showed the experiments, the amide group attacked the keto group to give intermediates **XIIIa** and **XIIIb** (Scheme 3) that wre stabilized by a process like a reaction of an acid cleavage of ethyl acetoacetate providing 9c-methyl-2-R^{3}-9b,9c-dihydro-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalene-1,3,4-triones **XIVa** and **XIVb**.

The composition and structure of compounds **XIVa** and **XIVb** were proved by elemental analysis, IR and ^{1}H NMR spectroscopy. The IR spectra contain characteristic absorption bands of carbonyls from lactone (1745) and lactam groups (1700–1705 and 1780–1790 cm^{-1}). In the ^{1}H NMR spectra characteristic signals were observed in the region (δ, ppm) 1.21–1.28 s and 3.10–3.50 s belonging to the protons of a methyl group and to a methine proton (CH) respectively.

The analogous stereochemical outcome was observed in the reaction of zinc enolates **IId** and **IIe** with *N,N*-disubstituted 2-oxochromen-3-carboxamides. The reaction proceeded through the formation of intermediate **XVIa** and **XVIb** to result in alkyl 3-{2-oxo-1a-(piperidinocarbonyl)- and 3-{6-R'-1a-(morpholinocarbonyl)-2-oxo-1-R^{1}-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-dimethyl-3-oxopropanoates **XVIIa** and **XVIIb** (Scheme 4).

The composition and structure of compounds **XVIIa** and **XVIIb** were proved by elemental analysis, IR and ^{1}H NMR spectroscopy. In the IR spectra of compound **XVIIa** and **XVIIb** appear the characteristic absorption bands of amide group carbonyl at 1645–1660 cm^{-1}, carbonyls of keto, lactone, and ester groups in the region 1710–1760 cm^{-1}. In the ^{1}H NMR spectrum the characteristic multiplet of the methine proton in the region 3.36–3.43 ppm testifies to the presence of a cyclopropane structural fragment. The chemical shift value of the alkyl group R, e.g., that equal to 1.08 ppm in compound **XVIIa**, suggests that in the isomer obtained of esters **XVIIa** and

Scheme 4.



XV, R' = H, X = CH_2 (**a**); R' = Br, X = O (**b**); **XVI, XVII**, R^1 = Alk = Me, R' = H, X = CH_2 (**a**); R^1 = Alk = Et, R' = Br, X = O (**b**).

XVIIb , like in compounds **XIIa** and **XIIb,** the position of the R substituent and the methine proton corresponds to the *E*-configuration.

EXPERIMENTAL

IR spectra were recorded on spectrometers UR-20 (**VIa–VId, IX, XIIa, XIIb, XVIIa**, and **XVIIb**) and Specord 75IR (**XIVa** and **XIVb**) from mulls of individual compounds in mineral oil. ^{1}H NMR spectra of compounds (**VIa–VId, IX, XIIa, XIVa, XVIIa**, and **XVIIb**) dissolved in $CDCl_3$ were registered on a spectrometer Tesla BS-576A (100 MHz), internal reference HMDS. NMR spectra of compound **XIVb** in $CDCl_3$ solution were measured on a spectrometer Mercury Plus-300 (300 MHz), internal reference TMS; spectrum of compound **XIIb** in $CDCl_3$ solution, on a spectrometer Bruker DRX-400 (400 MHz), internal reference TMS.

Alkyl 2,2-dialkyl-3-{1a-(R^3-carbamoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]-chromen-1-yl}-3-oxopropanoates VIa–VId. To 1.5 g of fine zinc turnings zinc in 8 ml of ether and 5 ml of ethyl acetate was added 0.023 mol of ethyl 2,2-dialkyl-4,4-dibromo-3-oxobutanoate in 3 ml of ethyl acetate. The mixture was boiled to nearly complete zinc dissolution. Then 0.01 mol of the primary 2-oxochromen-3-carboxamide was added, the mixture was heated for 40 min, cooled, and hydrolyzed with an acetic acid solution. The reaction products were extracted into ether, the extract was dried with Na_2SO_4, the solvents were distilled off, and the residue was recrystallized from methanol.

Ethyl 2,2-dimethyl-3-{1a-(4-methyl-phenyl-carbamoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]-chromen-1-yl}-3-oxopropanoate (VIa). Yield 43%, mp 154–156°C. IR spectrum, ν, cm^{-1}: 1685, 1720, 1740–1755, 3330. ^{1}H NMR spectrum, δ, ppm: 1.15 m (9H, 3CH_3), 2.21 s (3H, CH_3), 3.21 d, 3.77 d (2H, 2CH, ^3J 9.7 Hz), 4.05 q (2H, CH_2, *J* 7.4 Hz), 6.88–7.30 m (8H, C_6H_4, 4-$CH_3C_6\underline{H}_4$), 9.99 s (1H, NH). Found, %: C 68.80; H 59.71; N 3.07. $C_{25}H_{25}NO_6$. Calculated, %: C 68.95; H 5.79; N 3.22.

Ethyl 3-(1a-benzylcarbamoyl-2-oxo-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl)-3-oxo-2,2-diethylpropanoate (VIb). Yield 53%, mp 126–127°C. IR spectrum, ν, cm^{-1}: 1670, 1715, 1720–1740, 3365. ^{1}H NMR spectrum, δ, ppm: 0.38 t, 0.62 t, 1.12 t (9H, 3CH_3, *J* 7.4 Hz), 1.70 m (4H, 2CH_2), 3.09 d, 3.69 d (2H, 2CH, ^3J 9.9 Hz), 4.04 q (2H, CH_2, *J* 7.4 Hz), 4.37 d (2H, C$\underline{H}_2$Ph, *J* 8.4 Hz), 6.85–7.22 m (9H, C_6H_4, C_6H_5), 8.41 m (1H, NH). Found, %: C 69.82; H 6.21; N 2.88. $C_{27}H_{29}NO_6$. Calculated, %: C 69.96; H 6.31; N 3.02.

Ethyl 3-{1a-(4-methylphenylcarbamoyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]-chromen-1-yl}-3-oxo-2,2-diethylpropanoate (VIc). Yield 49%, mp 160–161°C. IR spectrum, ν, cm^{-1}: 1680, 1720, 1740–1760, 3325. ^{1}H NMR spectrum, δ, ppm: 0.35 t, 0.59 t, 1.12 t (9H, 3 CH_3, *J* 7.4 Hz), 1.67 q, 1.69 q (4H, 2CH_2, *J* 7.4 Hz), 2.21 s (3H, CH_3), 3.11 d, 3.73 d (2H, 2CH, ^3J 9.7 Hz), 4.02 q (2H, CH_2, *J* 7.4 Hz), 6.85–7.31 m (8H, $C_6\underline{H}_4$, 4-$CH_3C_6\underline{H}_4$), 9.95 s (1H, NH). Found, %: C 69.85; H 6.24; N 2.90. $C_{27}H_{29}NO_6$. Calculated, %: C 69.96; H 6.31; N 3.02.

Ethyl 3-oxo-3-(2-oxo-1a-cyclohexylcarbamoyl-1a,7b-dihydrocyclopropa[*c*]-chromen-1-yl)-2,2-

diethylpropanoate (VId). Yield 67%, mp 107–108°C. IR spectrum, ν, cm^{-1}: 1675, 1720, 1740–1760, 3380. ^{1}H NMR spectrum, δ, ppm: 0.37 t, 0.61 t, 1.17 t (9H, 3 CH_3, *J* 7.4 Hz), 1.67 m (4H, $2CH_2$), 1.10–1.93 m (10H, C_6H_{11}), 3.04 d, 3.66 d (2H, 2CH, ^3J 9.9 Hz), 3.67 m (1H, C_6H_{11}), 4.09 q (2H, CH_2, *J* 7.4 Hz), 6.87–7.52 m (4H, C_6H_4), 7.98 d (1H, NH, *J* 8.7 Hz). Found, %: C 68.44; H 7.19; N 2.97. $C_{26}H_{33}NO_6$. Calculated, %: C 68.55; H 7.30; N 3.07.

Alkyl 3-{1-R^1-1a-(morpholinocarbonyl)-2-oxo- and 3-{2-oxo-1a-(piperidinocarbonyl)-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-R^2,R^2-3-oxoalkanoates IX, XVIIa, and XVIIb. The procedure for preparation of compounds **IX, XVIIa,** and **XVIIb** is similar to the synthesis of compounds **VIa–VId** save that in the preparation of zinc enolate we used 0.013 mol of alkyl 2,2-dialkyl-4,4-dibromo-3-oxoalkanoate, and as substrates were used N-substituted 2-oxochromen-3-carboxamide and 6-bromo-2-oxochromen-3-carboxamide.

Ethyl 3-{6-bromo-1a-(4-morpholinocarbonyl)-2-oxo-1a,7b-dihydrocyclopropa[*c*]-chromen-1-yl}-3-oxo-2,2- diethylpropanoate (IX). Yield 64%, mp 165–167°C. IR spectrum, ν, cm^{-1}: 1660, 1705, 1740–1745. ^{1}H NMR spectrum, δ, ppm: 0.48 t, 0.62 t (6H, $2CH_2C\underline{H}_3$), 1.21 t (3H, $OCH_2C\underline{H}_3$), 1.65–1.90 m (4H, $2C\underline{H}_2CH_3$), 3.10–3.73 m (10H, 2CH, C_4H_8NO), 4.11 q (2H, $OC\underline{H}_2CH_3$), 6.86 d, 7.23 m (3H, C_6H_3). Found, %: C 55.11; H 5.35; N 2.60. $C_{24}H_{28}BrNO_7$. Calculated, %: C 55.18; H 5.40; N 2.68.

Methyl 2,2-dimethyl-3-{1-methyl-2-oxo-1a-(4-piperidinocarbonyl)-1a,7b-dihydro-cyclopropa-[*c*]chromen-1-yl}-3-oxopropanoate (XVIIa). Yield 57%, mp 195–196°C. IR spectrum, ν, cm^{-1}: 1660, 1705, 1740–1750. ^{1}H NMR spectrum, δ, ppm: 1.08 s (3H, CH_3), 1.00–1.65 m (6H, $C_5H_{10}N$), 1.39 s (3H, CH_3), 1.57 s (3H, CH_3), 3.00–3.70 m (4H, $C_5H_{10}N$), 3.43 s (1H, CH), 3.61 s (3H, $COOC\underline{H}_3$), 6.86–7.30 m (4H, C_6H_4). Found, %: C 66.74; H 6.52; N 3.31. $C_{23}H_{27}NO_6$. Calculated, %: C 66.81; H 6.58; N 3.39.

Ethyl 3-{6-bromo-1a-(4-morpholino-carbonyl)-2-oxo-1-ethyl-1a,7b-dihydrocyclopropa[*c*]chromen-1-yl}-2,2-dimethyl-3-oxopropanoate (XVIIb). Yield 51%, mp 181–182°C. IR spectrum, ν, cm^{-1}: 1645, 1710, 1730, 1760. ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, $CH_2C\underline{H}_3$), 1.09 t (3H, $OCH_2C\underline{H}_3$), 1.41–1.75 m (10H, $2CH_3$, $C\underline{H}_2CH_3$), 3.36 s (1H, CH), 3.22–3.84 m (8H, C_4H_8NO), 4.06 q (2H, $OC\underline{H}_2CH_3$), 6.80–7.70 m (3H, C_6H_3). Found, %: C 55.09; H 5.34; N 2.62. $C_{24}H_{28}BrNO_7$. Calculated, %: C 55.18; H 5.40; N 2.68.

Alkyl 2,2-dimethyl-3-oxo-3-{2-oxo-1a-(cyclohexylcarbamoyl)-1-ethyl-1a,7b-dihydrocyclopropa-[*c*]chromen-1-yl}propanoates XIIa and XIIb. The procedure for preparation of compounds **XIIa** and **XIIb** is similar to the synthesis of compounds **VIa–VId** save that in the preparation of zinc enolate we used alkyl 4,4-dibromo-2,2-dimethyl-3-oxohexanoates.

Methyl 2,2-dimethyl-3-oxo-3-(2-oxo-1a-cyclohexylcarbamoyl-1-ethyl-1a,7b-dihydro-cyclopropa-[*c*]chromen-1-yl)propanoate (XIIa). Yield 61%, mp 142–143°C. IR spectrum, ν, cm^{-1}: 1650, 1720–1740, 3360. ^{1}H NMR spectrum, δ, ppm: 072 t (3H, $C\underline{H}_3CH_2$), 1.05–1.98 m (15H, $CH_3C\underline{H}_2$, $OCH_2C\underline{H}_3$, C_6H_{11}), 1.45 s, 1.51 s (6H, $2CH_3$), 3.60 m (1H, C_6H_{11}), 3.62 s (3H, $COOCH_3$), 3.83 s (1H, CH), 6.89–7.43 m (4H, C_6H_4), 8.00 d (1H, NH). Found, %: C 67.93; H 7.01; N 3.11. $C_{25}H_{31}NO_6$. Calculated, %: C 68.01; H 7.08; N 3.17.

Ethyl 2,2-dimethyl-3-oxo-3-(2-oxo-1a-cyclohexylcarbamoyl-1-ethyl-1a,7b-dihydro-cyclopropa[*c*]chromen-1-yl)propanoate (XIIb). Yield 55%, mp 142–143°C. IR spectrum, ν, cm^{-1}: 1650, 1720–1740, 3360. ^{1}H NMR spectrum, δ, ppm: 0.74 t (3H, $C\underline{H}_3CH_2$, *J* 7.4 Hz), 1.07–1.99 m (15H, $CH_3C\underline{H}_2$, $OCH_2C\underline{H}_3$, C_6H_{11}), 1.42 s, 1.51 s (6H, $2CH_3$), 3.62 m (1H, C_6H_{11}), 3.87 s (1H, CH), 4.04 q (2H, $OC\underline{H}_2CH_3$, *J* 7.4 Hz), 6.83–7.41 m (4H, C_6H_4), 8.01 d (1H, NH, *J* 8.7 Hz). Found, %: C 68.42; H 7.28; N 2.94. $C_{26}H_{33}NO_6$. Calculated, %: C 68.55; H 7.30; N 3.07.

9b,9c-Dihydro-9C-methyl-2-R^3-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-1,3,4-triones XIVa and XIVb. To 0.01 mol of substituted 2-oxochromen-3-carboxamide was added 1 ml of THF and 1 ml of HMPA, then zinc enolate obtained by the reaction of 0.023 mol of methyl 4,4-dibromo-2,2-dimethyl-3-oxopentanoate, and 10 ml of ethyl acetate and 5 ml of ethyl ether. The reaction mixture was boiled for 40 min, cooled, and hydrolyzed with an acetic acid solution, the reaction products were extracted into ether, the extract was dried with Na_2SO_4, the solvents were distilled off, and the residue was recrystallized from methanol.

2-Benzyl-9b,9c-dihydro-9C-methyl-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]naphthalene-1,3,4-trione (XIVa). Yield 44%, mp 185–186°C. IR spectrum, ν, cm^{-1}: 1700, 1745, 1780. ^{1}H NMR spectrum, δ, ppm: 1.21 s (3H, CH_3), 3.10 s (1H, CH), 4.53 s (2H, CH_2), 6.85–7.30 m (9H, C_6H_4, C_6H_5). Found, %: C 71.95; H 4.48; N 4.09. $C_{20}H_{15}NO_4$. Calculated, %: C 72.06; H 4.54; N 4.20.

9b,9c-Dihydro-9c-methyl-2-(4-methylphenyl)-5-oxa-2-azacyclopenta[2,3]cyclopropa[1,2-*a*]-naphthalene-1,3,4-trione (XIVb). Yield 38%, mp 281–282°C. IR spectrum, ν, cm^{-1}: 1705, 1745, 1790. ^1H NMR spectrum, δ, ppm: 1.28 s (3H, CH_3), 2.29 s (3H, CH_3), 3.50 s (1H, CH), 7.05–7.35 m (9H, C_6H_4, 4-$MeC_6\underline{H}_4$). Found, %: C 71.93; H 4.47; N 4.11. $C_{20}H_{15}NO_4$. Calculated, %: C 72.06; H 4.54; N 4.20.

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