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Chemistry of Acyl(imidoyl)ketenes: IX.* Synthesis and Thermolysis of 3-Aroyl-8-chloro-1,2-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones

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Abstract—Reactions of 3-Z-aroylmethylene-6-chloro-3,4-dihydro-2*H*-1,4-benzoxazine-2-ones with oxalyl chloride afford 3-aroyl-8-chloro-1,2-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones and Z-3-(2-aryl-2-chlorovinyl)-6-chloro-2*H*-1,4-benzoxazine-2-ones. Aroyl(imidoyl)ketenes generated by decarbonylation of pyrrolobenzoxazinetriones undergo dimerization through [4+2]-cycloaddition to form 4-aroyl-3-aroyloxy-2-(2-oxo-2*H*-1,4-benzoxazin-3-yl)-1*H*,5*H*-pyrido[2,1-*c*][1,4]benzoxazine-1,5-diones.

The evolution of chemistry of acyl(imidoyl)ketenes is hampered by insufficient development of convenient methods for generation thereof from available initial compounds (unlike the chemistry of monosubstituted analogs, acyl ketenes and imidoyl ketenes) [2–5]. One of the simplest and the most available procedure for generating acyl(imidoyl)ketenes is thermal decarbonylation of 4-acyl-2,3(1*H*)-purrolediones. The main advantage of this method is the possibility of wide variation of substituents in initial pyrrolediones and consequently of generating versatile acyl(imidoyl)ketenes.

The thermolysis of 4-aroyl-2,3(1*H*)-pyrrolediones fused by the [*a*] side to 1,4-benzoxazin-2-ones results in generating aroyl(imidoyl)ketenes whose imidoyl fragment is a part of a heterocycle [6–8]. The synthesis of initial 3-aroyl-1,2-dihydro-4*H*-pyrrolo[2,1-*C*][1,4]benzoxazine-1,2,4-triones is performed by diacylation with oxalyl chloride of *Z*-3-aroylmethylene-3,4-dihydro-2*H*-1,4-benzoxazin-2-ones [9]. At the introduction of an NO_2 group into the position *6* of the initial 1,4-benzoxazin-2-one the reaction with oxalyl chloride yields instead of the expected 8-nitropyrrolobenzoxazinetrione the 6-nitro-*Z*-3-(2-phenyl-2-chlorovinyl)-2*H*-1,4-benzoxazin-2-one [10].

Our target was the synthesis of pyrrolobenzoxazinetriones with a chlorine atom in position *8*, their thermolysis for generation of acyl(imidoyl)ketenes, and evaluation of the features of these reactions compared to those of unsubstituted analogs.

The reaction of methyl 4-aryl-2-hydroxy-4-oxo-2-butenoates **Ia–Id** with 2-amino-4-chlorophenol and 2-aminophenol afforded 3-aroylmethylene-3,4-dihydro-2*H*-1,4-benzoxazin-2-ones **IIa–IIf** (Scheme 1). The physicochemical characteristics of compounds **IIa–IIf** are consistent with the published data on compounds of this class and evidence their existence as *Z*-isomers stabilized by an intramolecular hydrogen bond [9, 11–13].

The reaction of *Z*-3-aroylmethylene-3,4-dihydro-2*H*-1,4-benzoxazin-2-ones **IIa**, **IIb**, **IIe**, and **IIf** with oxalyl chloride in chloroform or dichloroethane solution furnished substituted 3-aroyl-1,2-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]-benzoxazine-1,2,4-triones **IIIa**, **IIIb**, **IIIe**, and **IIIf**.

Pyrrolobenzoxazinetriones **IIIa**, **IIIb**, **IIIe**, and **IIIf** are dark-violet crystalline substances soluble in dichloroethane, acetonitrile, insoluble in carbon tetrachloride and alkanes. The physicochemical characteristics of compound **IIIe** are in agreement with the previously published [9], the characteristics of pyrrolediones **IIIa**, **IIIb**, and **IIIf** are consistent with these data. Only the shift by 20 cm^{-1} to higher frequencies of the lactone carbonyl absorption band in the IR spectra of compounds **IIIa** and **IIIb** should be noted as compared with analogous pyrrolobenzoxazinetriones lacking a chlorine atom in position *8* [9].

*For communication VIII, see [1].

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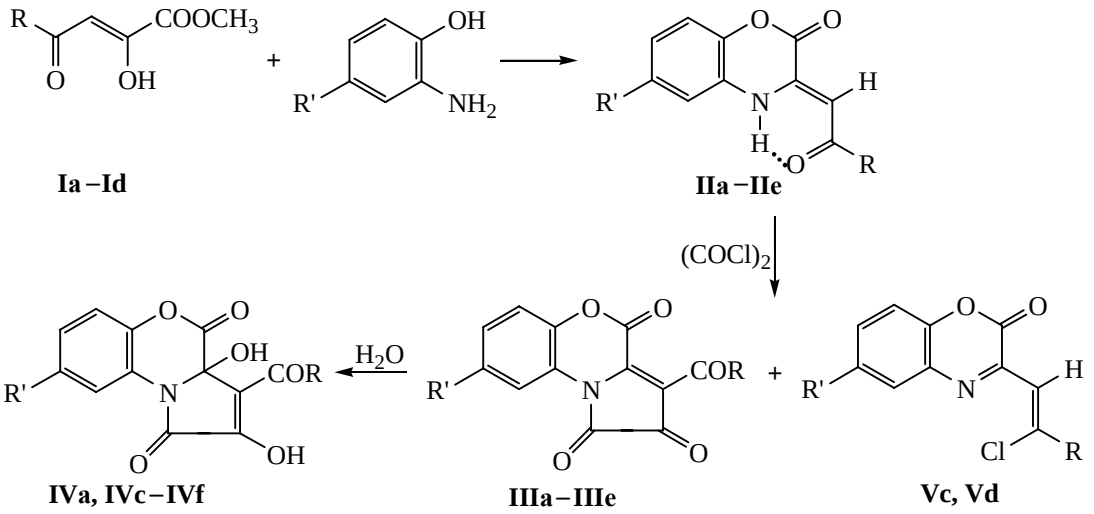
Scheme 1.



R' = Cl, R = C_6H_5 (a), *p*-ClC_6H_4 (**b**), *p*-$CH_3CH_2OC_6H_4$ (**c**), 3,4-$(CH_3O)_2C_6H_3$ (**d**); R' = H, R = *p*-ClC_6H_4 (**e**), 3,4-$(CH_3O)_2C_6H_3$ (**f**).

The solutions of pyrrolobenzoxazinetriones in inert solvents in contact with air lose the dark-violet color due to addition of water resulting in formation of 3-aroyl-2,3a-dihydroxy-1,3a-dihydro-4*H*-pyrrolo[2,1-*C*][1,4]-benzoxazine-1,4-diones **IV**. The latter are as a rule isolated from the mother liquor in the synthesis of pyrrolobenzoxazinetriones [9].

The reaction of oxalyl chloride with 8-chloro-1,4-benzoxazinones **IIc** and **IId** with electron-donor substituents in the aroyl moiety takes another route. Benzoxazinone **IId** in contrast to its nonchlorinated analog **IIf** under the same reaction conditions formed a product of oxygen substituion in aroyl fragment by chlorine, *Z*-3-[2-(3,4-dimethoxyphenyl)-2-chlorovinyl]-6-chloro-2*H*-1,4-benzoxazin-2-one (**Vd**). Although the reaction mixture during the process did not get black-violet, some pyrrolobenzoxazinetrione **IIId** still formed as evidenced by the isolation of its hydration product **IVd**.

Compound **Vd** is an orange crystalline substance. Its IR spectrum unlike that of the initial benzoxazinone **IId** lacks the absorption band of the aroyl group, and the band of the stretching vibrations of OCO group is displaced by 20 cm^{-1} to lower frequencies. The same pattern is observed in the IR spectrum of its analog with an NO_2 group in position *6* [10].

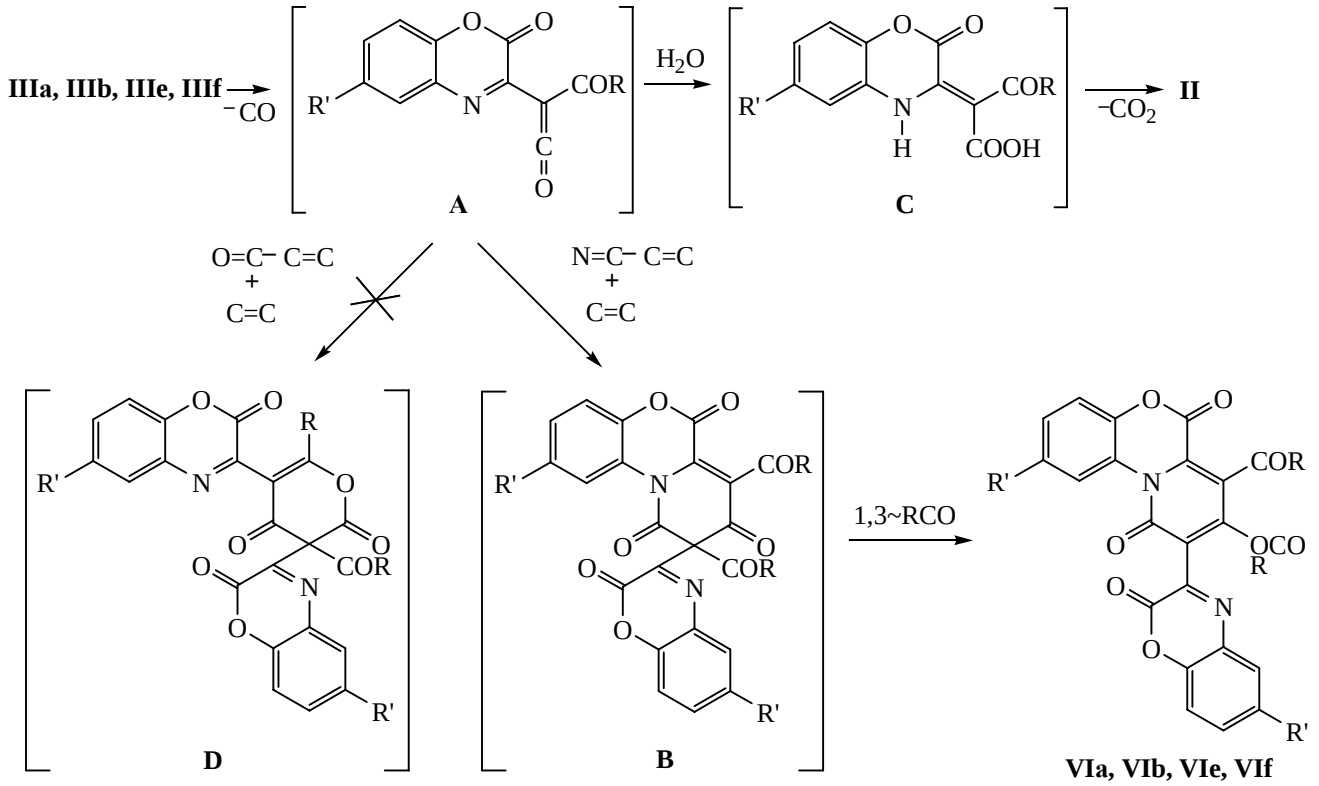
The reaction of benzoxazinone **IIc** with oxalyl chloride gave rise to a mixture of products. The violet color of the reaction mixture indicated the presence of the target pyrrolobenzoxazinetrione **IIIc** that was identified by its adduct with water **IVc**. Apart from compound **IVc** was isolated a mixture of benzoxazinone **IIc** (35%) and chlorostyrene derivative **Vc** (65%) as shown by spectral data and TLC.

The adducts of pyrrolobenzoxazinetriones with water **IVa**, **IVc–IVf** are crystalline substances of light-yellow color giving a positive test (cherry-brown color) for enol hydroxy group with an alcoholic solution of iron(III) chloride. Their IR spectra contain characteristic absorption bands: a narrow band of nonassociated hydroxy group in the region 3370–3415 cm^{-1} and a wide band of OH group involved in hydrogen bonds in the region 3100–3210 cm^{-1} in keeping with the known published data for this kind compounds [9, 14].

The thermolysis of pyrrolobenzoxazinetriones **IIIa**, **IIIb**, **IIIe**, and **IIIf** in inert aprotic solvents at 168–190°C resulted in formation of 4-aroyl-3-aroyloxy-2-(2-oxo-2*H*-1,4-benzoxazin-3-yl)-1*H*,5*H*-pyrido-[2,1-*c*][1,4]benzoxazine-1,5-diones **VIa**, **VIb**, **VIe**, and **VIf** (Scheme 2) due to [4+2]-cyclodimerization involving the imidoylketene moiety of generated aroyl(2-oxo-2*H*-1,4-benzoxazin-3-yl)ketenes **A** for diene and the ketene C=C bond as dienophile. The intermediately formed unstable dimers **B** are stabilized by 1,3-acylotropic rearrangement into pyridobenzoxazinetriones **VI** as was formerly shown by an example of acyl(imidoyl)ketene **A** possessing similar structure [R = 2,4,6-$(CH_3)_3C_6H_2$, R' = H] [8].

Compounds **VIa**, **VIb**, **VIe**, and **VIf** are yellow crystalline high-melting substances, sparingly soluble in the common organic solvents. The IR spectra of the thermolysis products contain a strong absorption band in the region 1735–1750 cm^{-1} originating from the

Scheme 2.



superimposed bands of stretching vibrations of three OCO bands belonging to aroyl and lactam carbonyl groups in the region 1655–1685 cm^{-1}, and stretching vibrations bands of the C=C and C=N bonds in the region 1590–1605 cm^{-1}. In the ^1H NMR spectra appears a characteristic downfield signal of the aromatic proton H^{10} in the range 9.1–9.3 ppm in a good agreement with existence of the interaction between the oxygen atom C^1=O and H^{10} hydrogen previously established by X-ray diffraction study on a similar in structure pyridobenzoxazinedione [8]. It should be mentioned that the integral intensity of this signal in the spectra of compounds **VIa**, **VIb**, **VIe**, and **VIf** is less than unity, although the overall intensity of all aromatic protons, including the downfield one, corresponds to their number. Apparently since the oxazine ring in the tricyclic system of compounds **VI** is not flat [6–8], some spatial isomers arise where the bond C^1=O···H–C^{10} does not exist.

Alongside compounds **VI** the thermolysis yielded benzoxazinones **II** as minor components of the reaction mixture whose presence was revealed by TLC. The latter may form by hydrolysis of the oxalyl fragment in the initial pyrrolobenzoxazinetriones, or via reaction of the generated acyl(imidoyl)ketene **A** with traces of water giving unstable acid **C** which decomposes in the course of thermolysis (Scheme 2). The second path involving the very reactive ketene **A** seems more probable for the former path requires more water, and we tried to exclude the presence of water during the experiment as much as possible.

The study performed showed that the presence of a chlorine atom in the position *6* of the substituted 3,4-dihydro-2*H*-1,4-benzoxazin-2-ones affected their reaction with oxalyl chloride; the electron-donor substituents in the 3-arylmethylidene fragment favored the formation of Z-*3*-(2-aryl-2-chlorovinyl)-2*H*-1,4-benzoxazin-2-ones and significantly reduced the yield of the target pyrrolobenzoxazinetriones. The introduction of chlorine does not affect the thermal decarbonylation of the pyrrolobenzoxazinetriones; the generated aroyl(2-oxo-2*H*-1,4-benzoxazin-3-yl)ketenes same as their unsubstituted analogs are stabilized by [4+2]-cyclodimerization where one molecule plays the role of dienophile with its C=C bond, and the second one acts as diene with the imidoylketene and not the alternative acylketene fragment (dimer **D,** Scheme 2).

EXPERIMENTAL

IR spectra of compounds obtained were recorded on a spectrophotometer UR-20 from mulls in mineral oil.

^{1}H NMR spectra were registered on spectrometers Bruker AM-300 and Bruker DRX-400 (internal reference TMS, solvent DMSO-d_6).

The reaction progress was monitored and the purity of compounds synthesized was checked by TLC on Silufol UV-254 plates.

Compounds **IIe–IVe** were previously described [9, 12].

***Z*-3-Phenacylidene-6-chloro-3,4-dihydro-2*H*-1,4-benzoxazin-2-one (IIa).** In 40 ml of dioxane were dissolved 2.32 g (10 mmol) of methyl benzoylpyruvate **Ia** and 1.75 g (10 mmol) of 2-amino-4-chlorophenol, and the mixture was boiled for 1 h 30 min. Then half of the solvent was distilled off, the separated precipitate was filtered off and recrystallized from toluene. Yield 2.2 g (60%), mp 213–215°C (publ.: mp 212–213°C [13]). IR spectrum, ν, cm^{-1}: 1640 (RCO), 1765 (OCO). ^{1}H NMR spectrum, δ, ppm: 6.93 s (1H, CH), 7.03–8.09 group of signals (7H, ArH), 7.80 s (1H, H^5), 12.60 s (1H, NH). Found, %: Cl 11.92; N 4.75. $C_{16}H_{10}ClNO_3$. Calculated, %: Cl 11.83; N 4.67.

***Z*-3-Aroylmethylene-3,4-dihydro-2*H*-1,4-benzoxazin-2-ones IIb–IId** were prepared similarly. Compound **IIb** was obtained from 4.5 g (18.7 mmol) of compound **Ib**. Yield 2.8 g (45%), mp 192–194°C. IR spectrum, ν, cm^{-1}: 1640 (RCO), 1765 (OCO). ^{1}H NMR spectrum, δ, ppm: 6.87 s (1H, CH), 7.13 d.d (1H, H^7, ^3J 8.8, ^4J 2.4 Hz), 7.25 d (1H, H^8, ^3J 8.8 Hz), 7.58 d.d (2H, H$^{3'}$, H$^{5'}$, ^3J6.8 Hz), 7.83 d (1H, H^5, ^4J 2.4 Hz), 8.01 d.d (2H, H$^{2'}$, H$^{6'}$, ^3J 6.8 Hz), 12.57 s (1H, NH). Found, %: Cl 21.14; N 4.28. $C_{16}H_9Cl_2NO_3$. Calculated, %: Cl 21.22; N 4.19.

Compound **IIc** was obtained from 3.0 g (12 mmol) of compound **Ic**. Yield 2.15 g (52%), mp 185–186°C. IR spectrum, ν, cm^{-1}: 1620 (RCO), 1765 (OCO). ^{1}H NMR spectrum, δ, ppm: 1.35 t (3H, CH_3, *J* 6.8 Hz), 4.12 q (2H, CH_2, *J* 6.8 Hz), 6.87 s (1H, CH), 7.05 d.d (2H, H$^{3'}$, H$^{5'}$, ^3J 8.4 Hz), 7.11 d.d (1H, H^7, ^3J 8.4, ^4J 2.4 Hz), 7.25 d (1H, H^8, ^3J 8.4 Hz), 7.78 d (1H, H^5, ^4J 2.4 Hz), 7.98 d.d (2H, H$^{2'}$, H$^{6'}$, ^3J 8.4 Hz), 12.54 s (1H, NH). Found, %: Cl 10.42; N 4.13. $C_{20}H_{18}ClNO_5$. Calculated, %: Cl 10.31; N 4.07.

Compound **IId** was obtained from 3.0 g (11.3 mmol) of compound **Id**. Yield 0.65 g (16%), mp 202–204°C. IR spectrum, ν, cm^{-1}: 1620 (RCO), 1750 (OCO). ^{1}H NMR spectrum, δ, ppm: 3.86 s (6H, OCH_3), 6.91 s (1H, CH), 7.11 group of signals (2H, H$^{2'}$, H$^{6'}$), 7.25 d (1H, H$^{5'}$, *J* 8.4 Hz), 7.52 d (1H, H^8, ^3J8.8Hz), 7.69 d.d (1H, H^7, ^3J 8.8, ^4J 2 Hz), 7.77 d (1H, H^5, ^4J 2 Hz), 12.60 s (1H, NH). Found, %: Cl 9.94; N 3.81. $C_{18}H_{14}ClNO_5$. Calculated, %: Cl 9.85; N 3.89.

***Z*-3-(3,4-Dimethoxybenzoylmethylene)-3,4-dihydro-2*H*-1,4-benzoxazin-2-one (IIf).** In 100 ml of dioxane were dissolved 5.95 g (22 mmol) of methyl 2-hydroxy-4-(3,4-dimethoxyphenyl)-4-oxo-2-butenoate **Id** and 2.44 g (22 mmol) of 2-aminophenol, the solution was boiled for 2 h 20 min, and half of the solvent was distilled off. The separated precipitate was filtered off and recrystallized from toluene. Yield 3.6 g (50%), mp 208–210°C. IR spectrum, ν, cm^{-1}: 1620 (RCO), 1735 (OCO). ^{1}H NMR spectrum, δ, ppm: 3.86 s (6H, 2CH_3), 6.88 s (1H, CH), 7.08–7.70 group of signals (7H, ArH), 12.82 s (1H, NH). Found, %: N 4.26. $C_{18}H_{15}NO_5$. Calculated, %: N 4.31.

3-Benzoyl-8-chloro-1,2-dihydro-4*H*-pyrrolo[2,1-*c*]-[1,4]benzoxazine-1,2,4-trione (IIIa) and 3-benzoyl-2,3a-dihydroxy-8-chloro-1,3a-dihydro-4*H*-pyrrolo[2,1-*c*]-[1,4]benzoxazine-1,4-dione (IVa). In a mixture of 25 ml of anhydrous dichloroethane and 17 ml of anhydrous chloroform was dissolved 2 g (6.7 mmol) of benzoxazinone **IIa**. Then 0.6 ml (7.0 mmol) of oxalyl chloride was added dropwise, and the mixture was boiled for 2 h with protection from atmospheric moisture. The solvent was distilled by half, the separated precipitate of compound **IIIa** was filtered off, and washed with chloroform. Yield 1.25 g (52%), mp 186–188°C. IR spectrum, ν, cm^{-1}: 1635 (RCO), 1670 (C^2=O), 1750 (NCO), 1795 (OCO). Found, %: Cl 9.94; N 4.05. $C_{18}H_8ClNO_5$. Calculated, %: Cl 10.02; N 3.96. The mother liquor was evaporated, and the residue was recrystallized from a mixture chloroform–hexane, 4:1. We obtained 0.08 g (3%) of compound **IVa**, mp 216–219°C. IR spectrum, ν, cm^{-1}: 1640 (PhCO), 1740–1760 (OCO, NCO), 3100–3200 br (OH ass.), 3380 (OH). Found, %: Cl 9.57; N 3.71. $C_{18}H_{10}ClNO_6$. Calculated, %: Cl 9.54; N 3.77.

3-(*p*-Chlorobenzoyl)-8-chloro-1,2-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione (IIIb). In 20 ml of anhydrous dichloroethane was dissolved 0.95 g (2.8 mmol) of benzoxazinone **IIb.** Then 0.26 ml (3.0 mmol) of oxalyl chloride was added dropwise, and the mixture was boiled for 1 h 30 min with protection from atmospheric moisture. The solvent was distilled by half, the separated precipitate of compound **IIIb** was filtered off, and washed with chloroform. Yield 0.77 g (70%), mp 202–203°C. IR spectrum, ν, cm^{-1}: 1640 (RCO), 1695 (C^2=O), 1730 (NCO), 1775 (OCO). Found,

%: Cl 18.22; N 3.74. $C_{18}H_7Cl_2NO_5$. Calculated, %: Cl 18.27; N 3.61.

3-(3,4-Dimethoxybenzoyl)-1,2-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-trione (IIIf) and 3-(3,4-dimethoxybenzoyl)-2,3a-dihydroxy-1,3a-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,4-dione (IVf) were synthesized by the same procedure. Compounds **IIIf** and **IVf** were obtained from 3.4 g (10.45 mmol) of compound **IIf**. Yield of compound **IIIf** 2.17 g (55%), mp 159–161°C. IR spectrum, ν, cm^{-1}: 1635 (RCO), 1660 (C^2=O), 1730 (NCO), 1765 (OCO). Found, %: N 3.75. $C_{20}H_{13}NO_7$. Calculated, %: N 3.69.

Yield of compound **IVf** 0.14 g (3%), decomp. at 138–140°C. IR spectrum, ν, cm^{-1}: 1660 (RCO), 1730 (NCO), 1770 (OCO), 3205–3260 br (OH ass.), 3370 (OH). ^{1}H NMR spectrum, δ, ppm: 3.81 s (3H, CH_3O), 3.86 s (3H, CH_3O), 6.81–7.55 group of signals (7H, ArH), 9.43, 11.70–13.50 br (OH). Found, %: N 3.51. $C_{20}H_{15}NO_8$. Calculated, %: N.53.

6-Chloro-*Z*-3-(2-chloro-2-*p*-ethoxyphenylvinyl)-2*H*-1,4-benzoxazine-2-one (Vc) and 2,3a-dihydroxy-8-chloro-3-(*p*-ethoxybenzoyl)-1,3a-dihydro-4*H*-pyrrolo[2,1-*c*][1,4]benzoxazine-1,4-dione (IVc). In 40 ml of anhydrous chloroform was dissolved 1.9 g (5.5 mmol) of benzoxazinone **IIc**. Then 0.5 ml (5.8 mmol) of oxalyl chloride was added dropwise, and the mixture was boiled for 2 h 40 min with protection from atmospheric moisture. The solvent was distilled by 2/3, the separated precipitate was filtered off and recrystallized from anhydrous chloroform. We obtained 0.24 g (10%) of compound **IVc**, mp 177–178°C. IR spectrum, ν, cm^{-1}: 1660 (RCO), 1735 (NCO), 1780 (OCO), 3200–3230 br (OH ass.), 3415 (OH). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3, *J*7.0Hz), 4.06 q (2H, CH_2, *J* 7.0 Hz), 6.83–7.95 group of signals (7H, ArH), 12.50 s (1H, OH). Found, %: Cl 8.64; N 3.49. $C_{20}H_{14}ClNO_7$. Calculated, %: Cl 8.53; N 3.37. From the mother liquor was additionally isolated 0.25 g of a mixture of compounds **IIc** and **Vc**, mp 150–156°C. IR spectrum, ν, cm^{-1}: 1765, 1730 sh, 1620 w. ^{1}H NMR spectrum, δ, ppm: 1.30 group of signals (CH_3), 4.08 group of signals (CH_2), 6.84 s (1H, CH in compound **IIc**), 6.88–7.75 group of signals (ArH), 12.50 s (1H, NH in compound **Vc**).

6-Chloro-*Z*-3-[2-(3,4-dimethoxyphenyl)-2-chlorovinyl]-2*H*-1,4-benzoxazin-2-one (Vd) and 3-(3,4-di-methoxybenzoyl)-2,3a-dihydroxy-8-chloro-1,3a-dihydro-4*H*-pyrrolo[2,1-*C*][1,4]benzoxazin-4-one (IVd) were obtained in the same way from 1.1 g (3.06 mmol) of compound **IId**. Yield of compound **Vd** 0.023 g (2%), mp 202–203°C. IR spectrum, ν, cm^{-1}: 1740 (C=O), 1590 (C=C, C=N). ^{1}H NMR spectrum, δ, ppm: 3.68 s (3H, OCH_3), 3.72 s (3H, OCH_3), 7.03–7.59 group of signals (6H, ArH), 7.77 d (1H, H^5, ^4J 2.7 Hz). Found, %: Cl 18.67; N 3.81. $C_{18}H_{13}Cl_2NO_4$. Calculated, %: Cl 18.75; N 3.70.

Yield of compound **IVd** 0.22 g (17%), mp 171–173°C. IR spectrum, ν, cm^{-1}: 1660 (RCO), 1730 (NCO), 1780 (OCO), 3210–3230 br (OH ass.), 3375 (OH). ^{1}H NMR spectrum, δ, ppm: 3.81 s (3H, CH_3O), 3.86 s (3H, CH_3O), 6.92–8.31 group of signals (6H, ArH), 9.87 s (1H, OH), 11.70–13.50 br (OH). Found, %: Cl 8.15; N 3.36. $C_{20}H_{14}ClNO_8$. Calculated, %: Cl 8.21; N 3.24.

4-Benzoyl-3-benzoyloxy-2-(2-oxo-6-chloro-2*H*-1,4-benzoxazin-3-yl)-9-chloro-1*H*,5*H*-pyrido[2,1-*C*][1,4]benzoxazine-1,5-dione (VIa). A solution of 0.3 g (0.9 mmol) of compound **IIIa** in 4 ml of Dowtherm A was heated for 5 min at 178–180°C. On cooling the separated precipitate was filtered off and recrystallized from toluene to obtain 0.12 g (40%) of compound **VIa**, mp 268–271°C. IR spectrum, ν, cm^{-1}: 1600, 1665, 1680, 1750, 1760. ^{1}H NMR spectrum, δ, ppm: 7.10–8.00 group of signals (ArH), 9.3 group of signals (H^{10}). Found, %: Cl 10.78; N 4.21. $C_{34}H_{16}Cl_2N_2O_8$. Calculated, %: Cl 10.88; N 4.30.

4-(*p*-Chlorobenzoyl)-3-(*p*-chlorobenzoyloxy)-2-(2-oxo-6-chloro-2*H*-1,4-benzoxazin-3-yl)-9-chloro-1*H*,5*H*-pyrido[2,1-*C*][1,4]benzoxazine-1,5-dione (VIb). A solution of 0.75 g (1.93 mmol) of compound **IIIb** in 3 ml of a mixture Dowtherm A–pseudocumene, 1:2, was boiled for 1 h at 185–187°C. On cooling the separated precipitate was filtered off and recrystallized from ethyl acetate. We obtained 0.2 g (29%) of compound **VIb**, mp 280–283°C (decomp.). IR spectrum, ν, cm^{-1}: 1585, 1605, 1680, 1750. ^{1}H NMR spectrum, δ, ppm: 7.42–8.01 group of signals (ArH), 9.27, 9.33 group of signals (H^{10}). Found, %: Cl 16.59; N 3.78. $C_{34}H_{14}Cl_4N_2O_8$. Calculated, %: Cl 16.69; N 3.89.

4-(*p*-Chlorobenzoyl)-3-(*p*-chlorobenzoyloxy)-2-(2-oxo-2*H*-1,4-benzoxazin-3-yl)-1*H*,5*H*-pyrido-[2,1-*c*]-[1,4]benzoxazine-1,5-dione (VIe) and 4-(3,4-dimethoxybenzoyl)-3-(3,4-dimethoxybenzoyloxy)-2-(2-oxo-2*H*-1,4-benzoxazin-3-yl)-1*H*,5*H*-pyrido-[2,1-*c*]-[1,4]benzoxazine-1,5-dione (VIf) were obtained in a similar way**.** Compound **VIe** was obtained from 1.0 g (2.83 mmol) of compound **IIIe**. Yield 0.65 g (35%), mp 296°C (decomp.). IR spectrum, ν, cm^{-1}: 1750, 1685, 1590. ^{1}H NMR spectrum, δ, ppm: 7.54 group of signals (15H, ArH), 9.03 group of signals (H^{10}). Found,

%: Cl 10.83; N 4.30. $C_{34}H_{16}Cl_2N_2O_8$. Calculated, %: Cl 10.88; N 34.30.

Compound **VIf** was obtained from 0.9 g (2.37 mmol) of compound **IIIf**. Yield 0.07 g (8%), mp 272–273°C. IR spectrum, ν, cm^{-1}: 1585, 1650, 1670, 1740 br. ^1H NMR spectrum, δ, ppm: 3.72 group of signals (12H, OCH_3), 6.78–7.75 group of signals (ArH), 9.14 d (H^{10}). Found, %: N 4.01. $C_{38}H_{26}N_2O_{12}$. Calculated, %: N 3.99.

REFERENCES

1. Maslivets, A.N., Aliev, Z.G., Krasnykh, O.P., Golovnina, O.V., and Atovmyan, L.O., *Khim. Geterotsikl. Soed.*, 2004, vol. 10, p. 1501.
2. Tidwell, T.T., *Ketenes*, New York: J. Wiley & Sons, Inc., 1995, 655 p.
3. Zhou, C. and Birney, D., *J. Am. Chem. Soc*., 2002, vol. 124, p. 5231.
4. Shumway, W.W., *Doctoral Sci. (Chem.) Dissertation*, Texas, Tech. University, 2001.
5. Wentrup, G., Heilmayer, W., and Kollenz, G., *Synthesis*, 1994, p. 1219.
6. Aliev, Z.G., Andreichikov, Yu.S., Krasnykh, O.P., and Atovmyan, L.O., *Izv. Akad. Nauk, Ser. Khim.*, 1993, p. 1633.
7. Aliev, Z.G., Krasnykh, O.P., Maslivets, A.N., Andreichikov, Yu.S., and Atovmyan, A.O., *Izv. Akad. Nauk, Ser. Khim*., 1999, p. 614.
8. Aliev, Z.G., Krasnykh, O.P., Maslivets, A.N., Andreichikov, Yu.S., amd Atovmyan, L.O., *Izv. Akad. Nauk, Ser. Khim*., 1999, p. 2154.
9. Maslivets, A.N., Mabrevskaya, I.V., Krasnykh, O.P., Burov, S.N., Andreichikov, Yu.S., *Zh. Org. Khim.*, 1992, vol. 28, p. 2545.
10. Aliev, Z. G., Krasnykh, O.P., Maslivets, A.N., and Atovmyan, L.O., *Izv. Akad. Nauk, Ser. Khim*., 2000, p. 2080.
11. Inagaki, T. and Iwanami, Y., *Org. Mass. Spectrometry*, 1977, p. 222.
12. Andreichikov, Yu. S., Voronova, L.A., and Kozlov, A.P., *Zh. Org. Khim.*, 1979, vol. 15, p. 520.
13. Iwanami, Y. and Seki, T., *Bull. Chem. Soc. Jpn*, 1971, vol. 44, p. 1316.
14. Aliev, Z.G., Krasnykh, O.P., Konyukhova, N.A., Maslivets, A.N., and Atovmyan, L.O., *Zh. Strukt. Khim*., 2001, vol. 42, p. 1008.