ISSN 1070-4280, Russian Journal of Organic Chemistry, 2020, Vol. 56, No. 8, pp. 1367–1373. © Pleiades Publishing, Ltd., 2020.
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Synthesis of Pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-triones by the Reaction of 3-Methylenemorpholin-2-ones with Oxalyl Chloride

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Received March 17, 2020; revised March 26, 2020; accepted March 30, 2020

Abstract—(*Z*)-3-(2-Aryl-2-oxoethylidene)morpholin-2-ones were synthesized by the reaction of aroylpyruvic acids with ethanolamine or 2-propanolamine. The products reacted with oxalyl chloride to form 8-aroyl-3,4-dihydropyrrolo[2,1-*c*][1,4]oxazin-1,6,7(1*H*)-triones.

Keywords: enaminoketone, 3-methylenemorpholin-2-one, pyrroloxazinetrione, oxalyl chloride, hetareno[*e*]pyrrole, 4-hetarylfurandione, X-ray diffraction

DOI: 10.1134/S1070428020080060

Heterocyclic enaminoketones react with oxalyl chloride to form hetareno[*e*]pyrrole-2,3-diones [1–13] or 4-heterylfuran-2,3-diones [14] or their mixture [15]. To obtain more evidence which would make it possible to predict what of the two mentioned directions would be realized, we synthesized substituted 3-methylenemorpholin-2-ones, representatives of a new class of heterocyclic enaminoketones, and studied their reaction with oxalyl chloride. The structure of the substituted morpholinones seems to be borderline for the realization of one of the alternative directions of the reaction with oxalyl chloride

Heating aroylpyruvic acids **1a**–**1f** with ethanolamine **2a** or 2-propanolamine **2b** in the presence of acetic acid in a 1 : 1 : 1 ratio in toluene with a Dean–Stark trap for 4–8 h (until water no longer evolved) gave (*Z*)-3-(2-aryl-2-oxoethylidene)morpholin-2-ones **3a–3k** (Scheme 1). The structure of compounds **3a**, **3e**, and **3i** was confirmed by X-ray diffraction (XRD) analysis. Compounds **3a–3c** were described earlier [16], which compounds **3d–3k** were synthesized for the first time. Under the conditions of synthesis of compounds **3a–3c** described in [16], specifically heating under reflux in 1,4-dioxane for 1–1.5 h) [16], we faced strong tarring of the reaction mixture and lower yields of products.

Compounds **3a–3k** are high-melting light yellow crystalline substances soluble in DMSO, DMF, acetone, ethyl acetate, chloroform, and 1,4-dioxane, sparingly soluble in aromatic hydrocarbons, and insoluble in alkanes and water.

The IR spectra of compounds **3a–3k** contain absorption bands of the NH bond (3198–3247 cm^{-1}, broad), lactam C^1=O group (1730–1744 cm^{-1}), and C=O group of the aroyl fragment (1615–1623 cm^{-1}).

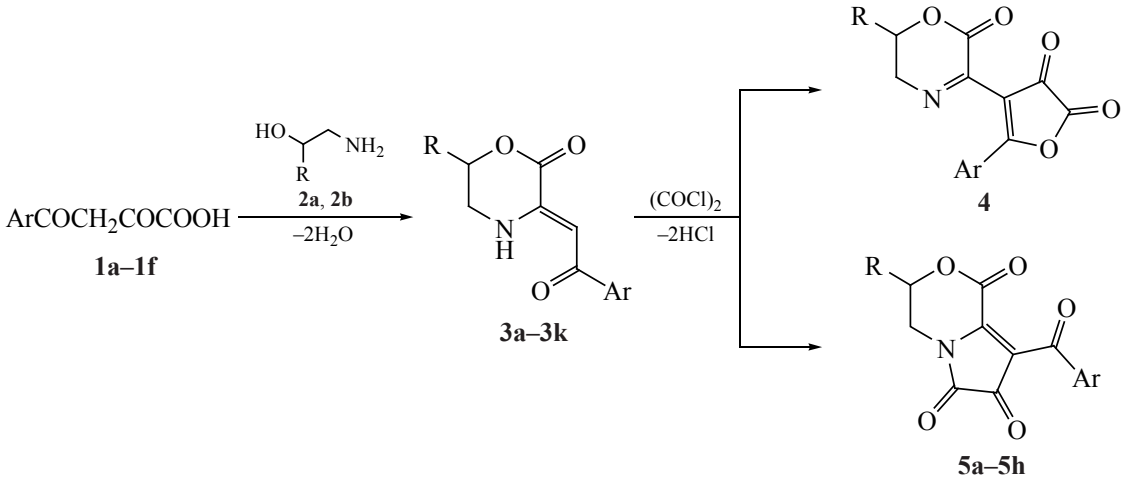
The ^{1}H NMR spectra of compounds **3a–3k** display, along with proton signals of the methylene groups of the morpholine ring and the aromatic rings and their substituents, a singlet of the methine proton (6.50–6.56 ppm) and a singlet of the NH proton (10.48–10.66 ppm).

The ^{13}C NMR spectra of compounds **3a–3k** show characteristic signals of the ketone carbonyl of the aroyl fragment (186.7–189.1 ppm) and lactam C^1=O group (160.1–160.8 ppm).

The reaction of compounds **3a–3k** with oxalyl chloride under the conditions usual for the synthesis of five-membered dioxaheterocycles (heating in anhydrous chloroform under reflux for 1–1.5 h) [17] afforded, instead of the expected 4-(2-oxo-5,6-dihydro-1,4-oxazin-3-yl)-5-arylfuran-2,3(2*H*)-diones **4**, 8-aroyl-3,4-dihydropyrrolo[2,1-*c*][1,4]oxazine-1,6,7(1*H*)-triones **5a–5h**[1] (Scheme 1).

[1] For preliminary communication, see [18].

Scheme 1.



1, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 4-MeC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**); **2**, R = H (**a**), Me (**b**); **3**, R = H, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 4-MeC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), 4-$NO_2C_6H_4$ (**f**), R = Me, Ar = Ph (**g**), 4-ClC_6H_4 (**h**), 4-BrC_6H_4 (**i**), 4-MeC_6H_4 (**j**), 4-$MeOC_6H_4$ (**k**); **5**, R = H, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 4-MeC_6H_4 (**d**), R = Me, Ar = Ph (**e**), 4-ClC_6H_4 (**f**), 4-BrC_6H_4 (**g**), 4-MeC_6H_4 (**h**).

Compounds **5a–5h** are high-melting red crystalline substances melting with decomposition, soluble in DMSO, DMF, acetone, acetonitrile, and 1,4-dioxane, sparingly soluble in aromatic hydrocarbons, ethyl acetate, and chloroform, and insoluble in alkanes and water.

The IR spectra of compounds **5a–5h** display stretching absorption bands of the lactam C^1=O and C^6=O groups (1749–1761 cm^{-1}), ketone C^6=O group (1716–1732 cm^{-1}), and the aroyl C=O group (1646–1673 cm^{-1}).

The ^{1}H NMR spectra of compounds **5a–5d** display, along with the proton signals of the aromatic rings and their substituents, signals of the 4-CH_2 (ppm) and 3-CH_2 groups of the oxazine ring at 3.82–3.83 and 4.71–4.72 ppm, respectively.

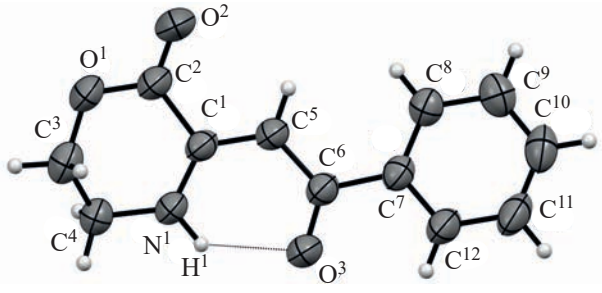


Fig. 1. General view of a molecule of (*Z*)-3-(2-oxo-2-phenylethylidene) morpholin-2-one (**3e**) by the XRD data (represented by 50% probability thermal ellipsoids).

The ^{13}C NMR spectra of compounds **5a–5h** show signals of the ketone carbonyls of the aroyl fragment (186.6–187.8 ppm) and the C^7=O group (180.8–181.5 ppm), lactam C^6=O (156.8–157.0 ppm) and C^1=O groups (154.8–155.0 ppm), as well as C^{8a} atom (138.8–148.5 ppm).

Apparently, the reaction of compounds **3** with oxalyl chloride occurs via closure of a pyrroledione ring because it is thermodynamically more stable that the alternative furandione ring. This reaction provides a new synthetic approach to the functionalized pyrrolo[2,1-*c*]oxazine-1,6,7-trione system.

In view of the poor understanding of the fine structure of 3-(2-aryl-2-oxoethylidene)morpholin-2-ones **3**, we performed an XRD analysis of these compounds.

Compounds **3a**, **3e**, and **3i** crystallize in centrosymmetricspace groups of the monoclinic or triclinic (compound **3i**) crystal systems (Figs. 1–3). The $C^4C^3C^5$ fragment of compound **3i** is disordered over two positions [minor component occupancy 0.22(3)] because the two enantiomers are present in the same position (in Fig. 3, the atoms of the minor component are not shown).

The molecules of all the three compounds have in general similar geometries. The oxazine rings have a *distorted boat* conformation, with the C^3 and O^1 (**3a**) and C^5 and O^3 atoms (**3e**) deviating by 0.81 and 0.29 Å and the C^3

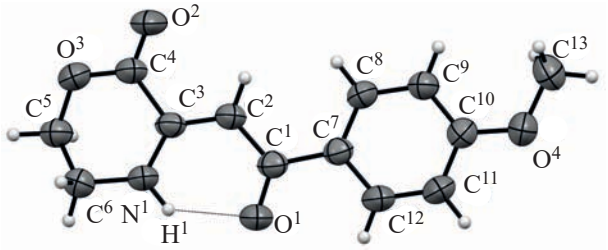


Fig. 2. General view of a molecule of (*Z*)-3-(2-(4-methoxyphenyl)-2-oxoethylidene)-6-methylmorpholin-2-one (**3e**) by the XRD data (represented by 50% probability thermal ellipsoids).

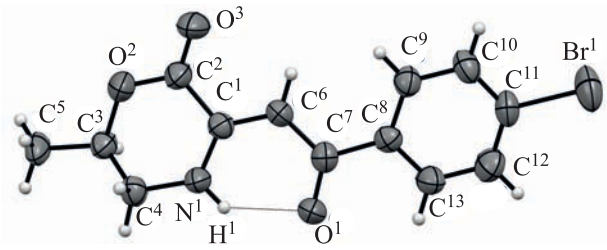


Fig. 3. General view of a molecule of (*Z*)-3-(2-(4-bromophenyl)-2-oxoethylidene)-6-methylmorpholin-2-one (**3i**) by the XRD data (represented by 50% probability thermal ellipsoids).

and O^2 atoms (**3i**), by 0.86 and 0.29 Å from the planes formed by the other ring planes. In all the compounds, the planar enaminoketone fragment formed by six-membered chelate rings by the intramolecular hydrogen bonds N^1–H^1···O^3 (**3a**) and N^1–H^1···O^1 (**3e** and **3i**). Therewith, the amino groups, too, are always involved in the formation of intramolecular hydrogen bonds (IHB). Thus, the molecules of compounds **3a** and **3i** in the crystals form cetrosymmetric fimers due to the IHBs N^1–H^1···O^3 [1–*x*, 1–*y*, 1–*z*] (**3a**) and N^1–H^1···O^1 [1–*x*, 1–*y*, 1–*z*] (**3i**). The molecules of compound **3e** in the crystal form infinite chains by the N^1–H^1···O^1 IHBs [*x*, *y*–1, *z*].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III HD 400 spectrometer (400 and 100 MHz, respectively), internal reference HMDS. The IR spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in mineral oil. The elemental analyses were obtained on a vario Micro cube analyzer. The purity of the synthesized compounds was confirmed by TLC on Merck Silica gel 60 F_{254} plates, eluents toluene, ethyl acetate, and toluene–ethyl acetate (5 : 1), vizualization by exposure to UV light (λ_{max} 254 nm).

The XRD analysis of compounds 3a, 3e, and 3i was performed on an Xcalibur Ruby single-crystal diffractometer with a CCD detector by a standard procedure (MoK_α-radiation, 295(2) K, ω scans, step 1°). Empirical absorption corrections were applied using SCALE3 ABSPACK algorithm [20]. The structures were decoded using SHELXS program [21] and refined by full-matrix least-squares on F^2 with anisotropic thermal factors for nonhydrogen atoms using SHELXL program [22] with OLEX2 graphic interface [23]. Hydrogen atoms (except for the OH and NH hydrogen refined independently with isotropic thermal factors) were included riding on their carrier atoms.

(*Z*)-3-(2-Oxo-2-phenylethylidene)morpholin-2-one (3a). Acetic acid, 7.44 mL (130.1 mmol), and 7.87 mL (130.1 mmol) of monoethanolamine were added to a solution of 25.00 g (130.1 mmol) of benzoylpyruvic acid in 300 mL of toluene. The mixture was refluxed with Dean–Stark trap for 6 h (until water no longer evolved), the solvent was removed, and the residue was recrystallized from ethyl acetate. Yield 89%, mp 128–130°C (EtOAc), 127–128°C [16]. IR spectrum, ν, cm^{-1}: 3236 br (NH), 1731 (C^1=O), 1616 (COPh). ^{1}H NMR spectrum, δ, ppm: 3.61 d.d (2H, C^4H_2, *J* 8.8, 5.0 Hz), 4.58 d.d (2H, C^3H_2, *J* 5.6, 4.8 Hz), 6.55 s (1H, CH=), 7.46–7.56 m ($3H_{arom}$), 7.90 d ($2H_{arom}$, *J* 6.9 Hz), 10.64 s (1H, NH). ^{13}C NMR spectrum , δ, ppm: 38.2, 67.3, 91.8, 126.9, 128.6, 131.7 138.9, 146.2, 160.5 (C^1=O), 189.1 (COAr). Found, %: C 66.09; H 5.29; N 6.66. $C_{12}H_{11}NO_3$. Calculated, %: C 66.35; H 5.10; N 6.45; O 22.10.

X-ray diffraction study of compound 3a. Monoclinic crystal system, space group $P2_1/n$, $C_{12}H_{11}NO_3$, *M* 217.22, *a* 6.7074(19), *b* 10.683(3), *c* 14.832(8) Å, β 92.75(3)°, *V* 1061.6(7) Å^3, *Z* 4, d_{calc} 1.359 g/cm^3; μ 0.099 mm^{-1}. Final divergence factors: R_1 0.0522 [for 1686 reflections with $I > 2\sigma(I)$], wR_2 0.1543 (for all 2512 unique reflections), *S* 1.050.

Compounds **3b–3k** were prepared similarly to compound **3a**.

(*Z*)-3-[2-(4-Chlorophenyl)-2-oxoethylidene]morpholin-2-one (3b). Yield 87%, mp 152–154°C (EtOAc), 153–154°C [16]. IR spectrum, ν, cm^{-1}: 3209 br (NH), 1731 (C^1=O), 1612 (COAr). ^{1}H NMR spectrum, δ, ppm: 3.62 d.d (2H, C^4H_2, *J* 8.6, 4.7 Hz), 4.58 t (2H, C^3H_2, *J* 5.1 Hz), 6.51 s (1H, CH=), 7.52 d ($2H_{arom}$, *J* 8.6 Hz), 7.90 d ($2H_{arom}$, *J* 8.5 Hz), 10.66 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 38.2, 67.2, 91.5, 128.7, 128.8, 136.6 137.5, 146.6, 160.4 (C^1=O), 187.6 (COAr). Found, %: C 57.47; H 4.25; N 5.30. $C_{12}H_{10}ClNO_3$.

Calculated, %: C 57.27; H 4.01; Cl 14.09; N 5.57; O 19.07.

(*Z*)-3-[2-(4-Bromophenyl)-2-oxoethylidene]morpholin-2-one (3c). Yield 88%, mp 156–158°C (EtOAc), 157–158°C [16]. IR spectrum, ν, cm^{-1}: 3242 br (NH), 1737 (C^1=O), 1620 (COAr). ^{1}H NMR spectrum, δ, ppm: 3.61 d.d (2H, C^4H_2, *J* 9.0, 4.9 Hz), 4.57 d.d (2H, C^3H_2, *J* 5.6, 4.8 Hz), 6.50 s (1H, CH=), 7.68 d ($2H_{arom}$, *J* 8.7 Hz), 7.83 d ($2H_{arom}$, *J* 8.8 Hz), 10.59 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 38.2, 67.2, 91.4, 125.5, 129.0, 131.6, 137.9, 146.4, 160.4 (C^1=O), 187.7 (COAr). Found, %: C 48.99; H 3.58; N 4.40. $C_{12}H_{10}BrNO_3$. Calculated, %: C 48.67; H 3.40; Br 26.98; N 4.73; O 16.21.

(*Z*)-3-[2-(4-Methylphenyl)-2-oxoethylidene]morpholin-2-one (3d). Yield 79%, mp 166–168°C (EtOAc). IR spectrum, ν, cm^{-1}: 3230 br (NH), 1739 (C^1=O), 1617 (COAr). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, CH_3), 3.60 d.d (2H, C^4H_2, *J* 8.8, 4.9 Hz), 4.57 d.d (2H, C^3H_2, *J* 5.6, 4.7 Hz), 6.54 s (1H, CH=), 7.28 d ($2H_{arom}$, *J* 7.6 Hz), 7.80 d ($2H_{arom}$, *J* 8.2 Hz), 10.59 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 21.0, 38.2, 67.3, 91.8, 127.0, 129.2, 136.3, 141.8, 146.0, 160.6 (C^1=O), 188.9 (COAr). Found, %: C 67.73; H 5.86; N 5.85. $C_{13}H_{13}NO_3$. Calculated, %: C 67.52; H 5.67; N 6.06; O 20.76.

(*Z*)-3-[2-(4-Methoxyphenyl)-2-oxoethylidene]morpholin-2-one (3e). Yield 75%, mp 175–177°C (EtOAc). IR spectrum, ν, cm^{-1}: 3243 br (NH), 1744 (C^1=O), 1620 (COAr). ^{1}H NMR spectrum, δ, ppm: 3.59 d.d (2H, C^4H_2, *J* 8.9, 4.9 Hz), 3.82 s (3H, OCH_3), 4.56 d.d (2H, C^3H_2, *J* 5.7, 4.9 Hz), 6.53 s (1H, CH=), 7.00 d ($2H_{arom}$, *J* 8.9 Hz), 7.88 d ($2H_{arom}$, *J* 8.9 Hz), 10.53 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 38.1, 55.3, 67.2, 91.7, 113.8, 128.9, 131.6, 145.6, 160.6 (C^1=O), 162.1, 188.1 (COAr). Found, %: C 63.53; H 4.98; N 5.88. $C_{13}H_{13}NO_4$. Calculated, %: C 63.15; H 5.30; N 5.67; O 25.88.

X-ray diffraction study of compound 3e. Monoclinic crystal system, space group $P2_1/n$, $C_{13}H_{13}NO_4$, *M* 247.24, *a* 14.043(6), *b* 6.4550(13), *c* 14.316(5) Å, β 113.73(4)°, *V* 1188.0(7) $Å^3$, *Z* 4, d_{calc} 1.382 g/cm^3; μ 0.103 mm^{-1}. Final divergence factors: R_1 0.0540 [for 1946 reflections with $I > 2\sigma(I)$], wR_2 0.1597 (for all 2936 unique reflections), *S* 1.049.

(*Z*)-3-[2-(4-Nitrophenyl)-2-oxoethylidene]morpholin-2-one (3f). Yield 35%, mp 267–269°C (EtOAc). IR spectrum, ν, cm^{-1}: 3202 br (NH), 3111, 3074 (NO_2), 1730 (C^1=O), 1623 (COAr). ^{1}H NMR spectrum, δ, ppm: 3.65 d.d (2H, C^4H_2, *J* 8.3, 5.4 Hz), 4.60 d.d (2H, C^3H_2, *J* 5.8, 4.7 Hz), 6.56 s (1H, CH=), 8.13 d ($2H_{arom}$, *J* 8.9 Hz), 8.31 d ($2H_{arom}$, *J* 8.9 Hz), 10.53 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 38.4, 67.1, 91.7, 123.8, 128.3, 144.0, 147.4, 149.1, 160.1 (C^1=O), 186.7 (COAr). Found, %: C 55.46; H 3.98; N 10.36. $C_{12}H_{10}N_2O_5$. Calculated, %: C 54.97; H 3.84; N 10.68; O 30.51.

(*Z*)-6-Methyl-3-(2-oxo-2-phenylethylidene)morpholin-2-one (3g). Yield 83%, mp 136–138°C (EtOAc). IR spectrum, ν, cm^{-1}: 3223 br (NH), 1737 (C^1=O), 1621 (COPh). ^{1}H NMR spectrum, δ, ppm: 1.35 d (3H, CH_3, *J* 6.3 Hz), 3.33–3.39 m, 3.62–3.67 m, 4.81–4.89 m (3H, NC<u>H</u>$_2$C<u>H</u>O), 6.55 s (1H, CH=), 7.49 t ($2H_{arom}$, *J* 7.3 Hz), 7.55 t ($1H_{arom}$, *J* 7.2 Hz), 7.90 d ($2H_{arom}$, *J* 6.9 Hz), 10.60 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.5, 43.5, 74.6, 91.6, 126.8, 128.5, 131.6, 138.8, 145.5, 160.6 (C^1=O), 189.0 (COAr). Found, %: C 67.90; H 5.25; N 6.34. $C_{13}H_{13}NO_3$. Calculated, %: C 67.52; H 5.67; N 6.06; O 20.76.

(*Z*)-3-[2-(4-Chlorophenyl)-2-oxoethylidene]-6-methylmorpholin-2-one (3h). Yield 84%, mp 156–158°C (EtOAc). IR spectrum, ν, cm^{-1}: 3247 br (NH), 1737 (C^1=O), 1615 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.35 d (3H, CH_3, *J* 6.4 Hz), 3.33–3.40 m, 3.62–3.68 m, 4.81–4.89 m (3H, NC<u>H</u>$_2$C<u>H</u>O), 6.51 s (1H, CH=), 7.53 d ($2H_{arom}$, *J* 8.6 Hz), 7.91 d ($2H_{arom}$, *J* 8.6 Hz), 10.61 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.6, 43.6, 74.7, 91.4, 128.7, 128.8, 136.6, 137.5, 146.0, 160.5 (C^1=O), 187.6 (COAr). Found, %: C 58.98; H 4.34; N 5.56. $C_{13}H_{12}ClNO_3$. Calculated, %: C 58.77; H 4.55; Cl 13.34; N 5.27; O 18.06.

(*Z*)-3-[2-(4-Bromophenyl)-2-oxoethylidene]-6-methylmorpholin-2-one (3i). Yield 87%, mp 170–172°C (EtOAc). IR spectrum, ν, cm^{-1}: 3232 br (NH), 1733 (C^1=O), 1615 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.35 d (3H, CH_3, *J* 6.4 Hz), 3.33–3.39 m, 3.62–3.68 m, 4.81–4.89 m (3H, NC<u>H</u>$_2$C<u>H</u>O), 6.51 s (1H, CH=), 7.68 d ($2H_{arom}$, *J* 8.7 Hz), 7.84 d ($2H_{arom}$, *J* 8.8 Hz), 10.62 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.5, 43.5, 74.6, 91.2, 125.4, 128.9, 131.5, 137.8, 145.9, 160.4 (C^1=O), 187.6 (COAr). Found, %: C 50.73; H 3.61; N 4.71. $C_{13}H_{12}BrNO_3$. Calculated, %: C 50.34; H 3.90; Br 25.76; N 4.52; O 15.48.

X-ray diffraction study of compound 3i. Triclinic crystal system, space group *P*–1, $C_{13}H_{12}BrNO_3$, *M* 310.15, *a* 6.9751(18), *b* 8.513(2), *c* 11.587(2) Å, α 79.891(19), β 73.58(2), γ 84.83(2)°, *V* 649.1(3) $Å^3$, *Z* 2, d_{calc} 1.587 g/cm^3, μ 3.166 mm^{-1}. Final divergence fac-

tors: R_1 0.0687 [for 1703 reflections with $I > 2\sigma(I)$], wR_2 0.1851 (for all 2997 unique reflections), S 1.037.

The results of the XRD analysis were deposited in the Cambridge Crystallographic Data Center under CCDC 1988255 (**3a**), 1988256 (**3e**), and 1988257 (**3i**) and are available by request at www.ccdc.cam.ac.uk/data_request/cif.

(*Z*)-6-Methyl-3-[2-(4-methylphenyl)-2-oxoethylidene]morpholin-2-one (3j). Yield 85%, mp 156–158°C (EtOAc). IR spectrum, ν, cm^{-1}: 3198 br (NH), 1737 (C^1=O), 1622 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.34 d (3H, CH_3, *J* 6.4 Hz), 2.35 s (3H, CH_3), 3.31–3.37 m, 3.60–3.66 m, 4.79–4.87 m (3H, NC$\underline{H}_2$C$\underline{H}$O), 6.54 s (1H, CH=), 7.28 d (2H_{arom}, *J* 8.6 Hz), 7.80 d (2H_{arom}, *J* 8.1 Hz), 10.55 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.5, 20.9, 43.5, 74.6, 91.6, 126.9, 129.0, 136.2, 141.7, 145.2, 160.6 (C^1=O), 188.8 (COAr). Found, %: C 68.88; H 5.95; N 5.98. $C_{14}H_{15}NO_3$. Calculated, %: C 68.56; H 6.16; N 5.71; O 19.57.

(*Z*)-3-[2-(4-Methoxyphenyl)-2-oxoethylidene]-6-methylmorpholin-2-one (3k). Yield 78%, mp 148–150°C (EtOAc). IR spectrum, ν, cm^{-1}: 3228 br (NH), 1731 (C^1=O), 1617 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.34 d (3H, CH_3, *J* 6.4 Hz), 3.30–3.36 m, 3.59–3.65 m, 4.79–4.87 m (3H, NC$\underline{H}_2$C$\underline{H}$O), 3.82 s (3H, OCH_3), 6.52 s (1H, CH=), 7.01 d (2H_{arom}, *J* 8.9 Hz), 7.88 d (2H_{arom}, *J* 8.9 Hz), 10.48 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.5, 43.5, 55.3, 74.6, 91.5, 113.8, 128.9, 131.5, 145.0, 160.8(C^1=O), 162.1, 188.1 (COAr). Found, %: C 64.13; H 5.90; N 5.67. $C_{14}H_{15}NO_4$. Calculated, %: C 64.36; H 5.79; N 5.36; O 24.49.

8-Benzoyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]-oxazine-1,6,7-trione (5a). A solution of 1.10 mL (12.7 mmol) oxalyl chloride in 5 mL of anhydrous chloroform was added in portions to a stirred solution of 2.297 g (10.6 mmol) of compound **3a** in 30 mL of anhydrous chloroform. The mixture was refluxed for 100 min and cooled. The red crystals that formed were filtered off and sried in a vacuum. Yield 95%, mp 216–218°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1750 (C^6=O, C^1=O), 1722 (C^7=O), 1646 (COPh). ^{1}H NMR spectrum, δ, ppm: 3.83 t (2H, C^4H_2, *J* 5.1 Hz), 4.72 t (2H, C^3H_2, *J* 5.0 Hz), 7.53 t (2H_{arom}, *J* 5.0 Hz), 7.68 t (1H_{arom}, *J* 7.4 Hz), 8.02 d (2H_{arom}, *J* 7.1 Hz). ^{13}C NMR spectrum, δ, ppm: 36.3 (C^4), 67.2 (C^3), 113.2, 128.6, 129.1, 134.0, 136.4, 148.1 (C^{8a}), 154.9 (C^1=O), 156.9 (C^6=O), 181.3 (C^7=O), 187.7 (COPh). Found, %: C 62.42; H 3.03; N 5.45. $C_{14}H_9NO_5$. Calculated, %: C 62.00; H 3.34; N 5.16; O 29.49.

Compounds **6b–6h** were prepared similarly to compound **6a**.

8-(4-Chlorobenzoyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5b). Yield 96%, mp 226–228°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1761 (C^6=O, C^1=O), 1718 (C^7=O), 1655 (COAr). ^{1}H NMR spectrum, δ, ppm: 3.83 t (2H, C^4H_2, *J* 5.1 Hz), 4.72 t (2H, C^3H_2, *J* 5.1 Hz), 7.60 d (2H_{arom}, *J* 8.8 Hz), 8.03 d (2H_{arom}, *J* 8.7 Hz). ^{13}C NMR spectrum, δ, ppm: 36.3 (C^4), 67.2 (C^3), 112.6, 128.8, 130.9, 135.3, 148.4 (C^{8a}), 154.9 (C^1=O), 156.9 (C^6=O), 165.2, 181.0 (C^7=O), 186.6 (COAr). Found, %: C 55.53; H 2.33; N 4.79. $C_{14}H_8ClNO_5$. Calculated, %: C 55.01; H 2.64; Cl 11.60; N 4.58; O 26.17.

8-(4-Bromobenzoyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5c). Yield 94%, mp 213–215°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1749 (C^6=O, C^1=O), 1716 (C^7=O), 1661 (COAr). ^{1}H NMR spectrum, δ, ppm: 3.83 t (2H, C^4H_2, *J* 5.2 Hz), 4.72 t (2H, C^3H_2, *J* 5.1 Hz), 7.74 d (2H_{arom}, *J* 8.5 Hz), 7.95 d (2H_{arom}, *J* 8.6 Hz). ^{13}C NMR spectrum, δ, ppm: 36.4 (C^4), 67.3 (C^3), 112.7, 128.4, 131.1, 131.8, 135.7, 148.5 (C^{8a}), 155.0 (C^1=O), 157.0 (C^6=O), 181.1 (C^7=O), 186.9 (COAr). Found, %: C 48.31; H 2.21; N 4.31. $C_{14}H_8BrNO_5$. Calculated, %: C 48.03; H 2.30; Br 22.82; N 4.00; O 22.85.

8-(4-Methylbenzoyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5d). Yield 90%, mp 210–212°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1755 (C^6=O, C^1=O), 1732 (C^7=O), 1655 (COAr). ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, CH_3), 3.82 t (2H, C^4H_2, *J* 5.1 Hz), 4.71 t (2H, C^3H_2, *J* 5.0 Hz), 7.29 d (2H_{arom}, *J* 7.8 Hz), 7.67 d (2H_{arom}, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 21.2 (C_6H_4-Me), 36.3 (C^4), 67.2 (C^3), 113.4, 128.6, 129.1, 134.1, 147.9 (C^{8a}), 154.9 (C^1=O), 156.9 (C^6=O), 164.9, 181.5 (C^7=O), 187.2 (COAr). Found, %: C 63.38; H 3.68; N 5.32. $C_{15}H_{11}NO_5$. Calculated, %: C 63.16; H 3.89; N 4.91; O 28.04.

8-Benzoyl-3-methyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5e). Yield 91%, mp 197–199°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1753 (C^6=O, C^1=O), 1732 (C^7=O), 1668 (COPh). ^{1}H NMR spectrum, δ, ppm: 1.44 d (3H, CH_3, *J* 6.4 Hz), 3.42 d.d (1H, C^4H_2, *J* 13.3, 9.6 Hz), 4.09 d.d (1H, C^4H_2, *J* 13.3, 9.6 Hz), 5.01 m (1H, C^3H_2), 7.53 t (2H_{arom}, *J* 7.8 Hz), 7.68 t (1H_{arom}, *J* 7.4 Hz), 8.01 d (2H_{arom}, *J* 7.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.4 (CH_3), 41.2 (C^4), 75.5 (C^3), 113.2,

128.6, 129.2, 134.0, 136.5, 147.5 (C^{8a}), 155.0 (C^1=O), 157.0 (C^6=O), 181.4 (C^7=O), 187.8 (COPh). Found, %: C 63.49; H 3.67; N 5.14. $C_{15}H_{11}NO_5$. Calculated, %: C 63.16; H 3.89; N 4.91; O 28.04.

3-Methyl-8-(4-chlorobenzoyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5f). Yield 83%, mp 206–208°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1750 (C^6=O, C^1=O), 1722 (C^7=O), 1671 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.44 d (3H, CH_3, *J* 6.4 Hz), 3.42 d.d (1H, C^4H_2, *J* 13.3, 9.6 Hz), 4.09 d.d (1H, C^4H_2, *J* 13.3, 3.1 Hz), 5.00 m (1H, C^3H_2), 7.60 d ($2H_{arom}$, *J* 8.6 Hz), 8.03 d ($2H_{arom}$, *J* 8.6 Hz). ^{13}C NMR spectrum, δ, ppm: 17.2 (CH_3), 41.0 (C^4), 75.3 (C^3), 112.4, 128.6, 130.8, 135.2, 138.8 (C^{8a}), 154.8 (C^1=O), 156.8 (C^6=O), 180.8 (C^7=O), 186.6 (COAr). Found, %: C 56.66; H 3.01; N 4.57. $C_{15}H_{10}ClNO_5$. Calculated, %: C 56.35; H 3.15; Cl 11.09; N 4.38; O 25.02.

8-(4-Bromobenzoyl)-3-methyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5g). Yield 86%, mp 223–225°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1754 (C^6=O, C^1=O), 1725 (C^7=O), 1673 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.45 d (3H, CH_3, *J* 6.4 Hz), 3.42 d.d (1H, C^4H_2, *J* 13.2, 9.5 Hz), 4.09 d.d (1H, C^4H_2, *J* 13.4, 3.0 Hz), 5.01 m (1H, C^3H_2), 7.74 d ($2H_{arom}$, *J* 8.1 Hz), 7.95 d ($2H_{arom}$, *J* 8.1 Hz). ^{13}C NMR spectrum, δ, ppm: 17.3 (CH_3), 41.2 (C^4), 75.4 (C^3), 112.6, 128.2, 130.9, 131.7, 135.7, 147.7 (C^{8a}), 154.9 (C^1=O), 156.9 (C^6=O), 181.0 (C^7=O), 186.9 (COAr). Found, %: C 49.79; H 2.56; N 4.08. $C_{15}H_{10}BrNO_5$. Calculated, %: C 49.48; H 2.77; Br 21.94; N 3.85; O 21.97.

3-Methyl-8-(4-methylbenzoyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine-1,6,7-trione (5h). Yield 75%, mp 179–181°C ($CHCl_3$). IR spectrum, ν, cm^{-1}: 1753 (C^6=O, C^1=O), 1724 (C^7=O), 1668 (COAr). ^{1}H NMR spectrum, δ, ppm: 1.45 d (3H, CH_3, *J* 6.4 Hz), 2.39 s (3H, CH_3), 3.43 d.d (1H, C^4H_2, *J* 13.3, 9.5 Hz), 4.07 d.d (1H, C^4H_2, *J* 13.3, 3.1 Hz), 5.01 m (1H, C^3H_2), 7.33 d ($2H_{arom}$, *J* 8.0 Hz), 7.91 d ($2H_{arom}$, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 17.4 (Me), 21.1 (C_6H_4–Me), 41.2 (C^4), 75.3 (C^3), 113.5, 129.2, 129.3, 134.1, 144.6, 147.2 (C^{8a}), 154.9 (C^1=O), 156.9 (C^6=O), 181.5 (C^7=O), 187.2 (COAr). Found, %: C 64.64; H 4.17; N 4.87. $C_{16}H_{13}NO_5$. Calculated, %: C 64.21; H 4.38; N 4.68; O 26.73.

FUNDING

The work was financially supported by the Russian Foundation for Basic Research (project no. 19-33-90222) and the Government of the Perm Krai.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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