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Five-Membered 2,3-Dioxo Heterocycles: LXXVII.* [4+2]-Cycloaddition of Alkyl Vinyl Ethers to 3-Aroylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4(4*H*)-triones

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Abstract—[4+2]-Cycloaddition of 3-aroylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4(4*H*)-triones to alkyl vinyl ethers gave substituted stereoisomeric (1*R**,16*R**)- and (1*S**,16*R**)-16-alkoxy-14-aryl-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-triones.

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Cycloaddition at conjugated multiple bonds in 4-acyl-2,3-dihydro-1*H*-pyrrole-2,3-diones fused to an isoquinoline fragment was extensively studied with a view to develop a strategy for building up heterocyclic system typical of *Erythrina* alkaloids [2, 3]. Thermal [4+2]-cycloaddition of polar C=C dienophiles at the conjugated C^5=C^4–C=O bond system of monocyclic 4-aroyl-substituted 1*H*-pyrrole-2,3-diones was reported to produce pyrano[4,3-*b*]pyrrole heterocyclic system [3–5]. Cycloaddition of olefins to 1*H*-pyrrole-2,3-diones fused to a 1,4-benzoxazin-2-one fragment, i.e., pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4(4*H*)-triones, was not studied previously.

We examined reactions of 3-aroylpyrrolo[2,1-*c*]-[1,4]benzoxazine-1,2,4(4*H*)-triones **Ia**–**If** with alkyl vinyl ethers **IIa** and **IIb**. Compounds **Ia**–**Id** were reported previously [6], while pyrrolobenzoxazinetriones **Ie** and **If** were synthesized for the first time by treatment of (3*Z*)-3-(-2-aryl-2-oxoethylidene)-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazin-2-ones **IIIa** and **IIIb** with oxalyl chloride. Compounds **IIIa** and **IIIb** were prepared in turn by reaction of 4-aryl-2,4-dioxobutanoic acids **IVa** and **IVb** with 2-aminophenols **Va** and **Vb**. The *Z* configuration of the exocyclic double bond in **IIIa** and **IIIb** is typical of such compounds; it followed from their spectral parameters [7].

By heating compounds **Ia**–**If** with alkyl vinyl ethers **IIa** and **IIb** at a ratio of 1:5 in boiling benzene (reaction time 20–60 min; until violet color of initial pyrrolobenzoxazinetriones **I** disappeared) we obtained representatives of a new class of difficultly accessible fused heterocyclic compounds, stereoisomeric (1*R**,16*R**)- and (1*S**,16*R**)-16-alkoxy-14-aryl-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-triones **VIa**–**VIh** [8] and **VIIa**–**VIIh**. Stereoisomers **VIa**–**VIh** were formed as major products, while minor stereoisomers **VIIa**–**VIIh** were not generally isolated; the latter gave rise to minor set of signals in the ^{1}H NMR spectra. Only in one case we succeeded in isolating by fractional crystallization pure diastereoisomers **VIh** and **VIIh**.

Stereoisomer mixtures **VIa**/**VIIa**–**VIh**/**VIIh** are yellow high-melting crystalline substances, which melt with decomposition and are readily soluble in DMSO and DMF, poorly soluble in other common organic solvents, and insoluble in saturated hydrocarbons and water. Isomers **VIIa**–**VIIh** are considerably better soluble in organic solvents and are characterized by higher R_f values than their isomers **VIa**–**VIh**.

The IR spectra of **VI**/**VII** contained absorption bands due to stretching vibrations of lactone carbonyl group (C^2=O, 1771–1802 cm^{-1}), lactam carbonyl group (C^{11}=O) and ketone carbonyl group (C^{12}=O, 1715–1731 cm^{-1}). Compounds **VIa**–**VIh** displayed in the ^{1}H NMR spectra signals from protons in aliphatic substituents and aromatic rings, as well as multiplet signals from the equatorial 16-H proton and methylene protons on C^{17} which give rise to an *ABX* spin system (δ 5.73–5.84 and 2.37–2.44 ppm, respectively). The

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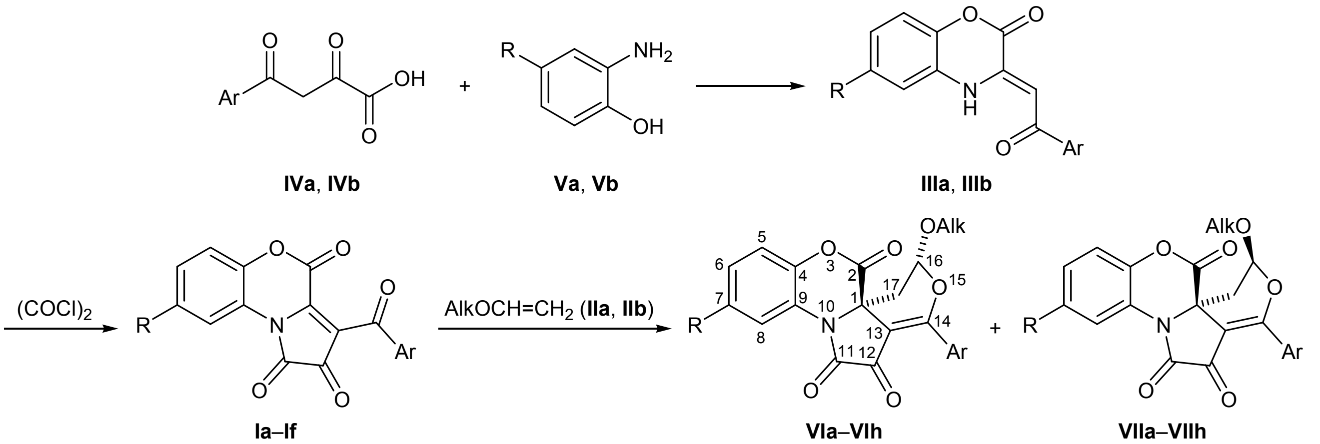
* For communication LXXVI, see [1].

Scheme 1.



I, Ar = Ph (**a**, **f**), 4-$EtOC_6H_4$ (**b**), 4-$MeOC_6H_4$ (**c**), 4-BrC_6H_4 (**d**), 4-$O_2NC_6H_4$ (**e**); R = H (**a**–**e**), Cl (**f**); **II**, Alk = Et (**a**), Bu (**b**); **III**, Ar = 4-$O_2NC_6H_4$ (**a**), Ph (**b**); R = H (**a**), Cl (**b**); **IV**, Ar = 4-$O_2NC_6H_4$ (**a**), Ph (**b**); **V**, R = H (**a**), Cl (**b**); **VI**, **VII**, Alk = Et (**a**, **d**–**h**), Bu (**b**, **c**); Ar = Ph (**a**, **b**, **h**), 4-$EtOC_6H_4$ (**c**, **f**), 4-$O_2NC_6H_4$ (**d**), 4-$MeOC_6H_4$ (**e**), 4-BrC_6H_4 (**g**); R = H (**a**–**g**), Cl (**h**).

16-H and 17-H signals of minor isomers **VIIa**–**VIIh** were located at δ 5.56–5.64 (16-H_{ax}), 2.13–2.26 (17-H_{ax}), and 2.61–2.79 ppm (17-H_{eq}) (*ABX*). The intensity ratio of signals from major isomers **VI** and minor isomers **VII** in the ^{1}H NMR spectra of the reaction mixtures was ~5 : 1.

Presumably, compounds **VIa**–**VIh** and **VIIa**–**VIIh** are formed as a result of participation of the O=C–C^3=C^{3a} conjugated bond system in 3-aroylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4(4*H*)-triones **Ia**–**If** in thermally initiated [4+2]-cycloaddition to the polarized C=C bond in alkyl vinyl ethers **IIa** and **IIb**. Predominant formation of stereoisomers **VIa**–**VIh** suggests that pseudoaxial orientation of the alkoxy group in the transition state for cycloaddition is more favorable.

EXPERIMENTAL

The IR spectra were recorded on an FSM-1201 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-400 spectrometer at 400 and 100 MHz, respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The purity of the synthesized compounds was checked by TLC on Silufol plates using benzene–ethyl acetate (5 : 1) and benzene as eluents.

(3*Z*)-[-2-(4-Nitrophenyl)-2-oxoethylidene]-3,4-dihydro-2*H*-1,4-benzoxazin-2-one (IIIa). A mixture of 1.0 mmol of 4-(4-nitrophenyl)-2,4-dioxobutanoic acid and 1.0 mmol of 2-aminophenol in 50 ml of propan-2-ol was heated for 90 min under reflux. After cooling, the orange precipitate was filtered off. Yield 89%, mp 245–247°C (from 1,4-dioxane). IR spectrum, ν, cm^{-1}: 3069 br (NH), 1758 (C^2=O), 1622 ($C^{2'}$=O). ^{1}H NMR spectrum, δ, ppm: 6.92 s (1H, CH), 7.17–8.37 m (8H, H_{arom}), 12.93 s (1H, NH). Found, %: C 61.82; H 3.21; N 9.15. $C_{16}H_{10}N_2O_5$. Calculated, %: C 61.94; H 3.25; N 9.03.

(3*Z*)-6-Chloro-3-(2-oxo-2-phenylethylidene)-3,4-dihydro-2*H*-1,4-benzoxazin-2-one (IIIb) was synthesized in a similar way. Yield 85%, mp 218–220°C (from toluene). IR spectrum, ν, cm^{-1}: 3071 br (NH), 1765 (C^2=O), 1622 ($C^{2'}$=O). ^{1}H NMR spectrum, δ, ppm: 6.93 s (1H, CH), 7.13–8.05 m (8H, H_{arom}), 12.62 s (1H, NH). Found, %: C 64.22; H 3.41; Cl 11.81; N 4.55. $C_{16}H_{10}ClNO_3$. Calculated, %: C 64.12; H 3.36; Cl 11.83; N 4.67.

3-(4-Nitrobenzoyl)pyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4(4*H*)-trione (Ie). A mixture of 1.0 mmol of compound **IIIa** and 1.1 mmol of oxalyl chloride in 70 ml of anhydrous benzene was heated for 110 min under reflux. The mixture was cooled, and the violet precipitate was filtered off. Yield 93%, mp 193–195°C. IR spectrum, ν, cm^{-1}: 1777 (C^4=O), 1737 (C^1=O, C^2=O), 1656 ($C^{1'}$=O). ^{1}H NMR spectrum, δ, ppm: 7.31–8.40 m (8H, H_{arom}). Found, %: C 59.42; H 2.28; N 7.53. $C_{18}H_8N_2O_7$. Calculated, %: C 59.35; H 2.21; N 7.69.

3-Benzoyl-8-chloropyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4(4*H*)-trione (If) was synthesized in a similar way. Yield 92%, mp 209–211°C. IR spectrum, ν, cm^{-1}: 1780 (C^4=O), 1738 (C^1=O, C^2=O), 1655 ($C^{1'}$=O). ^{1}H NMR spectrum, δ, ppm: 6.94–8.32 m (8H, H_{arom}). Found, %: C 61.23; H 2.38; Cl 10.06; N 3.89.

$C_{18}H_8ClNO_5$. Calculated, %: C 61.12; H 2.28; Cl 10.02; N 3.96.

(1*R,16*R**)-16-Ethoxy-14-phenyl-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIa) and (1*S**,16*R**)-16-ethoxy-14-phenyl-3,15-dioxa-10-azatetracyclo-[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIa) (**mixture of diastereoisomers at a ratio of ~10:3**).** A solution of 5.0 mmol of ethyl vinyl ether in 5 ml of anhydrous benzene was added to a solution of 1.0 mmol of compound **Ia** in 50 ml of anhydrous benzene. The mixture was heated for 40 min (until violet color typical of initial compound **Ia** disappeared) and cooled, and the precipitate was filtered off. Yield 89%, mp 236–239°C (decomp.). IR spectrum, ν, cm^{-1}: 1786 (C^2=O), 1724 (C^{11}=O, C^{12}=O). ^{1}H NMR spectrum, δ, ppm: **VIa**: 1.11 t (3H, CH_3, *J* = 7.0 Hz), 2.39 m (2H, 17-H), 3.72 m and 3.82 m (2H, OCH_2), 5.79 m (1H, CH), 7.34–7.95 m (9H, H_{arom}); **VIIa**: 1.21 t (3H, CH_3, *J* = 7.2 Hz), 2.19 m (1H, 17-H, *J* = 10.4, 12.8 Hz), 2.62 m (1H, 17-H, *J* = 4.2, 13.0 Hz), 3.82 m and 4.04 m (2H, OCH_2), 5.60 m (1H, CH, *J* = 4.0, 10.4 Hz), 7.34–7.85 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: **VIa**: 14.67 (Me), 38.88 (C^{17}), 54.48 (OCH_2), 65.65 (C^1), 100.33 (C^{16}), 102.86 (C^{13}), 116.68–143.10 (C_{arom}), 159.17 (C^{11}), 160.77 (C^2), 166.92 (C^{14}), 175.96 (C^{12}). Found, %: C 67.48; H 4.44; N 3.55. $C_{22}H_{17}NO_6$. Calculated, %: C 67.51; H 4.38; N 3.58.

Compounds **VIb–VIg** and **VIIb–VIIg** were synthesized in a similar way.

(1*R,16*R**)-16-Butoxy-14-phenyl-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIb) and (1*S**,16*R**)-16-butoxy-14-phenyl-3,15-dioxa-10-azatetracyclo-[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIb) (**mixture of diastereoisomers at a ratio of ~10:1**).** Yield 91%, mp 203–204°C (decomp.). IR spectrum, ν, cm^{-1}: 1788 (C^2=O), 1725 (C^{11}=O, C^{12}=O). ^{1}H NMR spectrum, δ, ppm: **VIb**: 0.83 t (3H, CH_3, *J* = 7.3 Hz), 1.29 m (2H, C**H**$_2$Me), 1.46 m (2H, C**H**$_2$Et), 2.40 t (2H, 17-H, *J* = 3.2 Hz), 3.67 m and 3.78 m (2H, OCH_2), 5.77 m (1H, CH), 7.33–7.93 m (9H, H_{arom}); **VIIb**: 0.89 t (3H, CH_3, *J* = 7.2 Hz), 1.37 m (2H, C**H**$_2$Me), 1.57 m (2H, C**H**$_2$Et), 2.18 m (1H, 17-H, *J* = 9.4, 12.6 Hz), 2.62 m (1H, 17-H, *J* = 4.4, 12.8 Hz), 3.80 m and 4.01 m (2H, OCH_2), 5.60 m (1H, CH, *J* = 4, 10.4 Hz), 7.33–7.85 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: **VIb**: 13.57 (Me), 18.37 (**C**H$_2$Me), 30.92 (**C**H$_2$CH$_2$Me), 38.88 (C^{17}), 54.46 (OCH_2), 69.05 (C^1), 100.67 (C^{16}), 102.81 (C^{13}), 116.68–143.13 (C_{arom}), 159.17 (C^{11}), 160.72 (C^2), 166.54 (C^{14}), 175.91 (C^{12}). Found, %: C 68.75; H 5.11; N 3.22. $C_{24}H_{21}NO_6$. Calculated, %: C 68.73; H 5.05; N 3.34.

(1*R,16*R**)-16-Butoxy-14-(4-ethoxyphenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]-heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIc) and (1*S**,16*R**)-16-butoxy-14-(4-ethoxyphenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIc) (**mixture of diastereoisomers at a ratio of ~10:1**).** Yield 88%, mp 186–188°C (decomp.). IR spectrum, ν, cm^{-1}: 1798 (C^2=O), 1728 (C^{11}=O, C^{12}=O). ^{1}H NMR spectrum, δ, ppm: **VIc**: 0.83 t (3H, CH_3, *J* = 7.4 Hz), 1.29 m (2H, C**H**$_2$CH$_3$), 1.39 t (3H, OCH$_2$C**H**$_3$, *J* = 7.0 Hz), 1.47 m (2H, C**H**$_2$CH$_2$CH$_3$), 2.38 m (2H, 17-H), 3.64 m and 3.79 m (2H, OCH_2), 4.17 m (2H, OC**H**$_2$CH$_3$), 5.73 m (1H, CH), 6.90–8.00 m (8H, H_{arom}); **VIIc**: 0.89 t (3H, CH_3, *J* = 7.2 Hz), 1.37 m (2H, C**H**$_2$CH$_3$), 1.39 t (3H, OCH$_2$C**H**$_3$, *J* = 7.0 Hz), 1.57 m (2H, C**H**$_2$CH$_2$CH$_3$), 2.19 m (1H, 17-H, *J* = 9.8, 13.0 Hz), 2.79 m (1H, 17-H, *J* = 4.2, 12.8 Hz), 3.66 m and 4.01 m (2H, OCH_2), 4.17 m (2H, OC**H**$_2$CH$_3$), 5.56 m (1H, CH, *J* = 4.0, 10.2 Hz), 6.90–7.88 m (8H, H_{arom}). Found, %: C 67.46; H 5.47; N 3.11. $C_{26}H_{25}NO_7$. Calculated, %: C 67.38; H 5.44; N 3.02.

(1*R,16*R**)-16-Ethoxy-14-(4-nitrophenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VId) and (1*S**,16*R**)-16-ethoxy-14-(4-nitrophenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIId) (**mixture of diastereoisomers at a ratio of ~5:3**).** Yield 87%, mp 236–240°C (decomp.). IR spectrum, ν, cm^{-1}: 1802 (C^2=O), 1731 (C^{11}=O, C^{12}=O). ^{1}H NMR spectrum, δ, ppm: **VId**: 1.11 t (3H, CH_3, *J* = 7.0 Hz), 2.42 m (2H, 17-H), 3.72 m and 3.82 m (2H, OCH_2), 5.84 m (1H, CH), 6.95–8.43 m (8H, H_{arom}); **VIId**: 1.21 t (3H, CH_3, *J* = 7.2 Hz), 2.26 m (1H, 17-H, *J* = 10.0, 13.2 Hz), 2.62 m (1H, 17-H, *J* = 3.8, 12.6 Hz), 3.81 m and 4.05 m (2H, OCH_2), 5.64 m (1H, CH, *J* = 4.0, 10.4 Hz), 6.95–8.34 m (8H, H_{arom}). Found, %: C 60.58; H 3.64; N 6.55. $C_{22}H_{16}N_2O_8$. Calculated, %: C 60.55; H 3.70; N 6.42.

(1*R,16*R**)-16-Ethoxy-14-(4-methoxyphenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIe) and (1*S**,16*R**)-16-ethoxy-14-(4-methoxyphenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIe) (**mixture of diastereoisomers at a ratio of ~5:1**).** Yield 93%, mp 234–236°C (decomp.). IR spectrum, ν, cm^{-1}: 1771 (C^2=O), 1715 (C^{11}=O, C^{12}=O). ^{1}H NMR spectrum, δ, ppm: **VIe**: 1.11 t (3H, $CH_2\mathbf{CH}_3$, J = 7.0 Hz), 2.37 m (2H, 17-H), 3.71 m and 3.81 m (2H, OCH_2), 3.90 s (3H, OCH_3), 5.75 m (1H, CH), 7.11–8.00 m (8H, H_{arom}); **VIIe**: 1.21 t (3H, Me, J = 7.0 Hz), 2.14 m (1H, 17-H, J = 10.4, 12.8 Hz), 2.61 m (1H, 17-H, J = 4.4, 13.2 Hz), 3.80 m and 4.06 m (2H, OCH_2), 3.90 s (3H, OCH_3), 5.58 m (1H, CH, J = 4.4, 10.4 Hz), 7.11–7.90 m (8H, H_{arom}). Found, %: C 65.59; H 4.57; N 3.35. $C_{23}H_{19}NO_7$. Calculated, %: C 65.55; H 4.54; N 3.32.

(1*R**,16*R****)-16-Ethoxy-14-(4-ethoxyphenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIf) and (1*S****,16*R****)-16-ethoxy-14-(4-ethoxyphenyl)-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIf) (**mixture of diastereoisomers at a ratio of ~10:1**).** Yield 91%, mp 202–204°C (decomp.). IR spectrum, ν, cm^{-1}: 1794 (C^2=O), 1728 (C^{11}=O, C^{12}=O). ^1H NMR spectrum, δ, ppm: **VIf**: 1.11 t (3H, CH_3, J = 7.0 Hz), 1.38 t (3H, 4′-$OCH_2\mathbf{CH}_3$, J = 7.0 Hz), 2.37 m (2H, 17-H), 3.71 m and 3.83 m (2H, 16-OCH_2), 4.18 q (2H, 4′-OCH_2, J = 6.9 Hz), 5.75 m (1H, CH), 7.10–8.00 m (8H, H_{arom}); **VIIf**: 1.21 t (3H, CH_3, J = 7.2 Hz), 1.38 t (3H, 4′-$OCH_2\mathbf{CH}_3$, J = 7.0 Hz), 2.13 m (1H, 17-H, J = 10.2, 12.8 Hz), 2.62 m (1H, 17-H, J = 4.2, 13.0 Hz), 3.83 m and 4.06 m (2H, 16-OCH_2), 4.18 q (2H, 4′-OCH_2, J = 6.9 Hz), 5.58 m (1H, CH, J = 4.0, 10.2 Hz), 7.10–7.89 m (8H, H_{arom}). Found, %: C 66.29; H 4.84; N 3.19. $C_{24}H_{21}NO_7$. Calculated, %: C 66.20; H 4.86; N 3.22.

(1*R**,16*R****)-14-(4-Bromophenyl)-16-ethoxy-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIg) and (1*S****,16*R****)-14-(4-bromophenyl)-16-ethoxy-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIg) (**mixture of diastereoisomers at a ratio of ~10:1**).** Yield 93%, mp 238–240°C (decomp.). IR spectrum, ν, cm^{-1}: 1794 (C^2=O), 1728 (C^{11}=O, C^{12}=O). ^1H NMR spectrum, δ, ppm: **VIg**: 1.11 t (3H, CH_3, J = 7.2 Hz), 2.38 m (2H, 17-H), 3.71 m and 3.82 m (2H, OCH_2), 5.78 m (1H, CH), 7.32–7.87 m (8H, H_{arom}); **VIIg**: 1.21 t (3H, CH_3, J = 7.0 Hz), 2.18 m (1H, 17-H, J = 10.2, 12.8 Hz), 2.61 m (1H, 17-H, J = 4.2, 13.0 Hz), 3.84 m and 4.04 m (2H, OCH_2), 5.62 m (1H, CH, J = 4.2, 10.2 Hz), 7.32–7.78 m (8H, H_{arom}). Found, %: C 55.98; H 3.48; Br 17.09; N 3.01. $C_{22}H_{16}BrNO_6$. Calculated, %: C 56.19; H 3.43; Br 16.99; N 2.98.

(1*R**,16*R****)-7-Chloro-16-ethoxy-14-phenyl-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraen-2,11,12-trione (VIh) and (16*S****,1*R****)-7-chloro-16-ethoxy-14-phenyl-3,15-dioxa-10-azatetracyclo[8.7.0.0^{1,13}.0^{4,9}]heptadeca-4,6,8,13-tetraene-2,11,12-trione (VIIh).** A solution of 5.0 mmol of ethyl vinyl ether in 5 ml of anhydrous benzene was added to a solution of 1.0 mmol of compound **If** in 50 ml of anhydrous benzene, and the mixture was heated for 20 min under reflux until violet color typical of initial compound **If** disappeared. The mixture was cooled, and the precipitate of stereoisomer **VIh** was filtered off. Yield 79%, mp 243–245°C (decomp.). IR spectrum, ν, cm^{-1}: 1788 (C^2=O), 1724 (C^{11}=O, C^{12}=O). ^1H NMR spectrum, δ, ppm: 1.11 t (3H, CH_3, J = 7.0 Hz), 2.44 m (2H, 17-H), 3.72 m and 3.82 m (2H, OCH_2), 5.80 m (1H, CH), 7.37–7.90 m (7H, H_{arom}). Found, %: C 62.21; H 3.80; Cl 8.21; N 3.25. $C_{22}H_{16}ClNO_6$. Calculated, %: C 62.05; H 3.79; N 3.29; Cl 8.33. The mother liquor was evaporated to dryness, the residue was ground with 10 ml of hexane, and the precipitate of stereoisomer **VIIh** was filtered off. Yield 12%, mp 237–239°C (decomp.). IR spectrum, ν, cm^{-1}: 1777 (C^2=O), 1730 (C^{11}=O, C^{12}=O). ^1H NMR spectrum, δ, ppm: 1.22 t (3H, CH_3, J = 7.0 Hz), 2.19 m (1H, 17-H, J = 4.2, 13.0 Hz), 2.68 m (1H, 17-H, J = 10.2, 13.0 Hz), 3.80 m and 4.06 m (2H, OCH_2), 5.60 m (1H, CH, J = 4.4, 10.0 Hz), 7.37–7.86 m (7H, H_{arom}). Found, %: C 62.17; H 3.72; Cl 8.36; N 3.38. $C_{22}H_{16}ClNO_6$. Calculated, %: C 62.05; H 3.79; Cl 8.33; N 3.29.

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