B. M. Krasovitskii, A. V. Yudashkin, I. V. Lysova, L. Sh. Afanasiadi, and A. E. Lipkin UDC 547.787.2.07:535.37:542.953

The corresponding 4-hetarylidene-2-aryloxazol-5-ones were synthesized by condensation of furyl- and thienyl-containing aldehydes with hippuric acid and substituted hippuric acids via the Erlenmeyer-Plöchl reaction. The electronic absorption and fluorescence spectra of the compounds in toluene were investigated.

A study of the electronic absorption and fluorescence spectra of a number of 4-arylidene-2-aryloxazol-5-ones (I) enabled us to conclude that the electronic interaction of the arylidene grouping with the carbonyl group of the oxazolone ring has a decisive effect on their color and the fluorescence intensity [1]:



This conclusion is in agreement with quantum-mechanical calculations of the electron structures of their molecules by the self-consistent field method within the π -electron approximation with the Pariser-Parr-Pople parametrization. An examination of the molecular diagrams of the ground and first excited states makes it possible to conclude that the electronic excitation is localized in the arylideneoxazolone fragment. According to the calculations, an aromatic grouping in the 2 position should not have a substantial effect on the long-wave absorption band.*

This is in agreement with our experimental data, except for those compounds that have strong electron-acceptor substituents in this aromatic grouping.

Continuing our search for organic luminophores among oxazolone derivatives we synthesized hetarylidene analogs of I and investigated their spectral-luminescence properties (II-IV, Het = 2-furyl, 2-thienyl, and 2,2'-dithienyl):



Compounds II-IV were synthesized via the Erlenmeyer-Plöchl reaction [2] by condensation of aromatic and heterocyclic aldehydes with hippuric acid and its heteroanalogs in glacial acetic acid in the presence of anhydrous sodium acetate.

The starting compounds for the synthesis of II and IV were 2-furoyl- and 2-thenoylglycines, which we obtained by acylation of glycine with pyromuic and thiophene-2-carboxylic acid chlorides in an alkaline medium at room temperature in analogy with [3].

*The authors thank B. Ya. Simkin for performing the quantum-mechanical calculations.

All-Union Scientific-Research Institute of Single Crystals, Kharkov 310059. V. V. Kuibyshev Kuibyshev Polytechnic Institute, Kuibyshev 443645. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1624-1627, December, 1979. Original article submitted April 17, 1979.

1303

	All and a second second second				in the second				
Com- pound	R	RI	°c',	Absorption, λ_{\max} nm $(\varepsilon \cdot 10^{-4})$	Fluores- cence, λ_{max} , nm at 77 K	S found,	Empirical formula	S calc.,	Yield,
la Ib Ila IIb	Phenyl 4-Biphenylyl Phenyl Phenyl	Phenyl Phenyl 2-Furyl 2-Thienyl		360 (3,9) 390 (4,45) 370 (4,35) 395 (3,42) 380 (3,74)	425 460 435, 465 450, 480		 C ₁₄ H ₉ O ₃ N C ₁₄ H ₉ O ₂ NS		
II _C IIIa IIIb	4-Styryl 2-Furyl 2-Thienyl	2-Thienyl Phenyl Phenyl	214 173 a 182b	295 (1,35) 405 (5,10) 390 (4,5) 410 (3,98) 300	485, 515 460, 490 460, 495	11,2 12,6	C ₁₆ H ₁₁ O ₂ NS — C ₁₄ H ₉ O ₂ NS	11,4 12,5	53 86 33
III c III d	2-Vinyl- thienyl 2-Vinylfuryl	Phenyl Phenyl	164 160	(infl) 395 (3,54) 290 (1,33) 420 (4,65) 410 (4,85)	525, 565 505, 545	11,2 5,1C	C16H11O2NS C16H11O3N	11,4	17 50
III e IV a	2,2'-Dithien- 5-yl 2-Furyl	Phenyl 2-Furyl	165 212	440 (5,20) 300 (1,54) 455 (4,88) 395 (7,39) 415 (7 13)	545, 565 465, 495	17,5 4,5 ^{°C}	C ₁₈ H ₁₁ O ₂ NS ₂ C ₁₂ H ₇ O ₄ N	17,6 4.5 [°]	27 60
IV b IV c	2-Thienyl 2,2'-Dithien- 5-yl	2-Thienyl 2-Thienyl	179 186	290 (0,85) 405 (3,28) 315 (2,08) 465 (6,45)	475, 510 555	24,4 27,3	C12H6O2NS2 C16H9O2NS3	24,1 27,7	57 14

TABLE 1. Characteristics of the Synthesized Compounds

^aAccording to the data in [8], this compound has mp 170°C. ^bAccording to the data in [9], this compound has mp 175°C. ^cAnalysis for the nitrogen content.

The structure of the synthesized compounds was confirmed by a study of the IR spectra. Intense bands corresponding to C=N stretching vibrations ($\nu_{C=N}$) at 1610 cm⁻¹ and C=O stretching vibrations ($\nu_{C=O}$) at 1680 cm⁻¹ appear in the spectrograms. In addition, bands of outof-plane vibrations of the hydrogen atoms of a trans-vinylene group at 955 cm⁻¹ and the characteristic bands of five-membered heterorings are observed in the IR spectra.

The presence of various groupings in the 4 position of the oxazol-5-one molecule makes the formation of geometrical isomers possible. When the new oxazol-5-ones were heated in acetone with iodine, which is generally used for the cis-trans isomerization of compounds with double bonds, no changes in their melting points were observed. The structures of the products that were isolated were identified by means of their UV and IR spectra. The absorption maxima of the starting substances and the substances isolated after such treatment coincide, and the absorption intensities do not change; this confirms their trans structure.

The spectral-luminescence characteristics of toluene solutions of II-IV are presented in Table 1. The character of the absorption and fluorescence curves of two of them is shown in Fig. 1.

The absorption spectra of toluene solutions of II-IV have a vibrational structure, and splitting of the long-wave band into two bands of approximately equal intensities is observed in the case of compounds that contain a furyl residue. A shortwave band at 290-315 nm appears in the case of compounds with one or two thienyl residues.

As a consequence of a change in the aromatic character of the grouping, replacement of the phenyl residue in the arylidene grouping of I by a heteroring leads to a significant bathochromic shift (30-35 nm) of the long-wave band, and the character of the heteroring has a substantial effect on its position and intensity (compare IIIa and IIIb, IIIc and IIId, and IVa and IVb). Compounds that contain a furan ring absorb in the longer-wave region and more intensely than their thiophene analogs. This increase in the probability of a long-wave electron transition is evidently a consequence of reinforcement of the "diene" properties of the furyl grouping as compared with the phenyl ring.

The increase in the length of the conjugation chain when a second vinylene group attached to a furyl or thienyl grouping is introduced in the 4 position of oxazol-5-one (IIIc and IIId) is accompanied by a further bathochromic shift of the absorption maxima.



Fig. 1. Absorption (a) and fluorescence (b) spectra in toluene: 1) 2-(2-fury1)-4-benzylideneoxazol-5-one (IIa); 2) 2-(2thieny1)-4-benzylideneoxazol-5-one (IIb).

This effect is reinforced significantly when the 2-thienyl grouping is replaced by a 2,2'-dithien-5-yl grouping and reaches 60 nm. This bathochromic shift of the absorption band of IIIe is due in all likelihood not only to an increase in the π -electron system when two conjugated thienyl groupings are introduced in the hetarylidene part of the molecule (compare IIIb and IIIe) but also to intensification of its electron-donor properties. The legitimacy of this assumption is confirmed by a comparison of the spectral characteristics of IIIe and its π -isoelectronic analog Ib. Replacement of the 4-biphenylyl grouping by a 2,2'-dithien-5-yl grouping gives rise to a 65 nm bathochromic shift of the long-wave absorption band. The electron-donor character of the thiophene ring was noted during an in-vestigation of the UV and IR spectra [4, 5], the dipole moments [6], and the basicity constants [7] of α , β -unsaturated ketones with a thienyl grouping.

In conformity with quantum-mechanical calculations of compounds that contain a substituent in the 4 position of the oxazolone ring, more significant bathochromic and hyperchromic effects are observed when one compares the spectral characteristics of 2- and 4-substituted oxazol-5-ones with heterocyclic substituents (IIa, IIb, IIIa, and IIIb) and 2-phenyl-4-benzylideneoxazol-5-one (Ia).

Most of the synthesized 4-hetarylideneoxazol-5-ones fluoresce intensely when they are irradiated with UV light in the solid state. At 77°K intense fluorescence is observed in the case of toluene solutions of all of the compounds described, and IIb fluoresces even at room temperature. As in the case of I, a distinctly expressed vibrational structure appears in the fluorescence spectra of frozen solutions of II-IV. The bathofluoric effect produced when various heterocyclic groupings are introduced increases in the same order as the bathochromic effect in the absorption spectra.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds (c $3 \cdot 10^{-3}$ mole/liter) were measured with an SF-4 spectrophotometer, and the fluorescence spectra were obtained with an apparatus consisting of a ZMR-3 monochromator, an FEU-18 photomultiplier, and an M-95 microammeter. The photoluminescence was excited with an SVDSH-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated with a DMR-4 monochromator. The IR spectra of KBr pellets of the compounds at 700-4000 cm⁻¹ were measured with a UR-20 spectrometer.

2-Furoyl- and 2-Thenoylglycines. A solution of sodium hydroxide (0.02 mole) and 0.011 mole of the chloride of the corresponding heterocyclic acid were added with vigorous stirring in the course of an hour to 0.01 mole of an aqueous solution of glycine in such a way that the solution remained constantly weakly alkaline. The mixture was then poured into hydro-chloric acid, and the precipitate was recrystallized from water to give white acicular crystals.

2-Furoylglycine, with mp 165°C, was obtained in 75% yield. Found: N 8.11%. C₇H₇O₄N. Calculated: N 8.3%. The UV spectrum contained an absorption maximum at 255 nm (ε 17800).

2-Thenoylglycine, with mp 172°C, was obtained in 81% yield. Found: S 17.1%. $C_7H_7O_3NS$. Calculated: S 17.3%. The UV spectrum contained an absorption maximum at 250 nm (ε 11900).

The 4-hetarylidene-2-aryl (hetaryl) oxazol-5-ones were obtained by the method described in [1] and were purified by recrystallization from heptane.

The yields, melting points, and results of analysis of the synthesized compounds are presented in Table 1.

LITERATURE CITED

- B. M. Krasovitskii, I. V. Lysova, and L. Sh. Afanasiadi, Khim. Geterotsikl. Soedin., No. 2, 158 (1978).
- 2. J. Plöchl, Ber., <u>16</u>, 2815 (1883).
- 3. A. Ingersoll and S. Babcock, Organic Syntheses [Russian translation], Collective Vol. 2, IL, Moscow (1949), p. 158.
- 4. V. F. Lavrushin, S. V. Tsukerman, and V. M. Nikitchenko, Zh. Obshch. Khim., <u>32</u>, 2677 (1962).
- 5. S. V. Tsukerman, A. I. Artemenko, V. F. Lavrushin, and Yu. S. Rozum, Zh. Obshch. Khim., 34, 2309 (1964).
- 6. S. V. Tsukerman, A. I. Artemenko, and V. F. Lavrushin, Zh. Obshch. Khim., <u>34</u>, 3591 (1964).
- 7. S. V. Tsukerman, L. A. Kutulya, V. M. Nikitchenko, and V. F. Lavrushin, Zh. Obshch. Khim., 33, 3180 (1963).
- 8. R. Andresano and S. Agnelo, Gazz. Chim. Ital., <u>85</u>, 374 (1955).
- 9. R. I. Gibbs, S. N. Timasheff, and F. F. Nord, J. Am. Chem. Soc., <u>73</u>, 5877 (1951).

SYNTHESIS OF SUBSTITUTED OXAZOLIDINONES FROM COMPOUNDS OF

THE ETHYLENE SERIES

V. B. Mochalin and N. I. Filenko

UDC 457.787.1.07

The reaction of N-bromocarbamates with ethylene compounds was investigated, and the high structural specificity of this reaction was demonstrated. The structures of the β -bromocarbamates obtained were confirmed by their IR and PMR spectra. When they are heated to 60-130°C, they are readily cyclized to the corresponding oxazo-lidinones.

2-Oxazolidinones are valuable starting compounds for the stereoselective synthesis of amino alcohols [1, 2]. In the present research we demonstrated the possibility of the synthesis of substituted oxazolidinones by the addition of N-bromocarbamates to ethylene compounds with subsequent pyrolysis of the resulting β -bromocarbamates. The reaction proceeds via the scheme



III^a, IV a $R = R^2 = R^3 = H$, $R^1 = CN$; IIIb, IVb $R = R^1 = H$, $R^2 = R^3 = -(CH_2)_4 -$; IIIc, IVc $R = R^2 = R^3 = H$, $R^1 = C_6H_5$; IIId, IVd $R = CH_3$, $R^2 = R^3 = H$, $R^1 = C_6H_5$; IIIe, IVe $R = R^2 = CH_3$, $R^1 = C_6H_5$, $R^3 = H$

M. V. Lomonosov Moscow Institute of Fine Chemical Technology, Moscow 119831. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1628-1630, December, 1979. Original article submitted December 11, 1978.