SYNTHESIS AND TRANSFORMATIONS OF 3-AROYLANTHRA[1,9-cd]ISOXAZOL-6-ONES

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3-Aroylanthra[1,9-cd]isoxazol-6-ones (II) are formed when 1-azido-2-aroylanthraquinones are reflexed in o-dichlorobenzene; this may constitute evidence that reactions of this type proceed via a "concerted" mechanism. Thermolysis of these and other substances in nitrobenzene leads to 7,8-phthaloylacridones, the structures of which were confirmed by alternative synthesis.

o-Azido carbonyl compounds are converted to isoxazoles when they are heated or irradiated [1]. Dyall [2] feels that the cyclization of 1-azido-2-acylbenzenes proceeds via a pericyclic mechanism that includes the simultaneous cleavage of the N—N bond and the formation of an O—N bond. Moreover, it is assumed [3] that the initial step is intramolecular 1,3-dipolar addition of the azido group to the carbonyl group to give a two-ring intermediate, which then rapidly eliminates a molecule of nitrogen to give a 2,1-benzisoxazole. It seemed of interest to us to study the cyclization of 1-azido-2-aroylanthraquinones (I), which contain, in the ortho positions relative to the azido group, a carbonyl group that tends to undergo cyclization via a "concerted" mechanism (the carbonyl group in the 9 position) and a carbonyl group that tends to undergo cyclization via a 1,3-dipolar addition mechanism (the carbonyl group of the aroyl substituent in the 2 position).

Azides Ia-d (Table 1) were synthesized via the usual scheme: amine → diazonium salt → azide. The thermolysis of Ia-d, which was carried out in refluxing o-dichlorobenzene, leads exclusively to 3-aroylanthra[1,9-cd]-isoxazol-6-ones (IIa-d) (Table 2).

The structures of isoxazoles IIa-d were confirmed by alternative synthesis of IIb by

TABLE 1. 1-Azido-2-aroylanthraquinones

Compound	mp, °C	λ_{max}, nm (lg ε)	N found, %	Empirical formula	N calc., %	Yield, %
Ia	87—88	335 (3,62)	11,8	$C_{21}H_{11}N_3O_3$	11,9	91
Ib	99—100	335 (3,63)	11,3	$C_{22}H_{13}N_3O_3$	11,4	95
Ic	122—123	335 (3,65)	10,7	$C_{21}H_{10}ClN_3O_3$	10,8	98
Id	115—116	335 (3,64)	9,9	$C_{21}H_{10}BrN_3O_3$	9,7	95

TABLE 2. 3-Aroylanthra[1,9-cd]isoxazol-6-ones

Compound	mp, °C	λ_{max}, nm (lg ε)	N found, %	Empirical formula	N calc., %	Yield, %
IIa	248—250	323 (4,18) 470 (3,79)	4,4	$C_{21}H_{11}NO_3$	4,3	92
IIb	261—263	323 (4,24) 475 (3,86)	4,1	$C_{22}H_{13}NO_3$	4,1	94
IIc	300—302	325 (4,22) 468 (3,84)	3,9	$C_{21}H_{10}ClNO_3$	3,9	97
IId	285—287	325 (4,19) 468 (3,79)	3,8	$C_{21}H_{10}BrNO_3$	3,5	96

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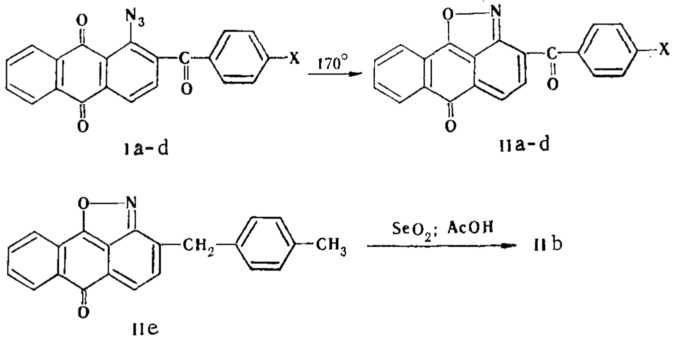
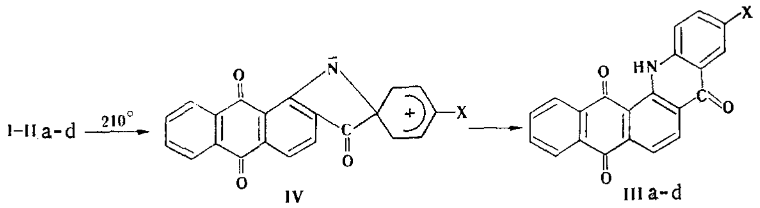
oxidation of 3-(p-methylbenzyl)anthra[1,9-cd]isoxazol-6-one (IIe) with selenium dioxide in acetic acid. The characteristics of the UV spectra of isoxazoles IIa, c, d are similar to those of IIb (Table 2). A broad band of stretching vibrations of carbonyl groups at 1670-1685 cm^{-1} is observed in the IR spectra of IIa-d, and absorption of a C=N bond is observed at 1620 cm^{-1}.

The formation of cyclization products IIa-d and the absence of competitive cyclization of the azido group with the carbonyl group in the 2 position of starting Ia-d constitutes evidence, in our opinion, in favor of the pericyclic mechanism. In fact, effective mesomeric interaction between the azido group and the carbonyl group in the 9 position promotes the realization of a reaction mechanism of this sort. In addition, the rigidly fixed position of this group virtually excludes the possibility of intramolecular 1,3-dipolar addition of the azido group to it. Moreover, the aroyl substituent in the 2 position of starting Ia-d, which, as a consequence of unhindered rotation about the C—C bond, has a tendency to undergo 1,3-dipolar addition, does not participate in this cyclization.



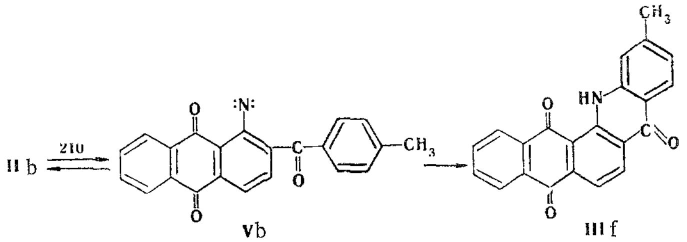
I-II a X=H; b X=CH$_3$; c X=Cl; d X=Br

We observed that isoxazolones IIa-d are converted to 7,8-phthaloylacridones (IIIa-d) when they are refluxed in nitrobenzene. The same compounds were obtained directly by refluxing azides Ia-d in nitrobenzene. It is characteristic that the formation of IIIa-d from isoxazolones IIa-d takes place under more severe conditions (210°C) than the recyclization of 3-arylthio- and 3-aryloxyanthra[1,9-cd]isoxazol-6-ones to 5,6-phthalylphenothiazines and 5,6-phthalylphenoxazines [4, 5]. The latter is probably explained by the increased electrophilicity of the aroyl substituent in the 3 position of IIa-d and, consequently, by the unfavorable conditions for the formation of spirocyclic intermediate IV. The formation of such intermediates was postulated in a study of the recyclization of 3-aryl[2,1]benzisoxazoles to acridones [6], but, as in the transformations that we studied, it was not possible to isolate or observe them under such severe conditions. The confirmed (by alternative synthesis) position of substituents X in IIIb-d serves as evidence in favor of reaction through intermediate IV (see the experimental section).



III a X=H; b X=CH$_3$; c X=Cl; d X=Br

The spectral characteristics of quinacridone, which was synthesized by cyclization of 1-(4-bromophenylamino)enthraquinone-2-carboxylic acid [7], were in complete agreement with the characteristics of IIId. At the same time, two singlet signals of methyl groups (2.8 and 2.9 ppm) with an integral intensity ratio of 2:1 are observed in the PMR spectrum (99% D_2SO_4) of the substance obtained by recyclization of isoxazole IIb. The signal of the methyl group in the spectrum of the quinacridone obtained by cyclization of 1-(p-toluidino)anthraquinone-2-carboxylic acid is found at 2.8 ppm. On the basis of the results obtained in this research it may be assumed that the recyclization of IIb proceeds both through the formation of a spiro intermediate of the IV type and by direct incorporation of nitrene Vb in the C—H bond, which leads to quinacridone IIIf.



Let us note that Meth-Cohn has presented similar results [8]: a mixture of 2-methyl- and 3-methylacridones in a ratio of 2:1 was obtained in the cyclization of 2-azido-4-methylbenzophenone; this is also explained by cyclization of 2-nitreno-4-methylbenzophenone both through a spiro intermediate and by direct insertion of the nitrene in the C–H bond.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-75 spectrometer. The UV spectra of solutions in toluene were recorded with a Specord UV-Vis spectrophotometer. The PMR spectra of solutions in D_2SO_4 were recorded with a Tesla BS-467 spectrometer (60 MHz). The chemical shifts were reckoned relative to the signal of the solvent (δ 10.9 ppm for $HDSO_4$) [9]. The course of the reaction and the purity of the substances were monitored by thin-layer chromatography (TLC) in a toluene–acetone system on Silufol UV-254 plates.

1-Azido-2-aroylanthraquinones (Ia-d). A solution of 0.01 mole of 1-amino-2-aroylanthraquinone [10] in 75-100 ml of acetic acid was diazotized at 20-25°C with a solution of nitrosylsulfuric acid prepared from 0.83 g (0.012 mole) of $NaNO_2$ and 10 ml of 95% H_2SO_4. After 15-20 min, the mixture was diluted with 50-60 ml of water, and 0.78 g (0.012 mole) of NaN_3 was added to the cooled (to 5-10°C) solution of the diazonium salt. The reaction mixture was maintained in the dark for 10-15 min, after which the precipitated azide was removed by filtration, washed with water, and dried at 20-30°C in the dark.

3-Aroylanthra[1,9-cd]isoxazol-6-ones (IIa-d). A solution of 0.01 mole of 1-azido-2-aroylanthraquinones was refluxed in 20-30 ml of o-dichlorobenzene for 5-10 min. Isoxazolones IIa-d were isolated from the cooled (to 0-5°C) reaction mixtures by filtration and washed with 10-15 ml of hexane.

7,8-Phthaloylacridones (IIIa-d). A solution of 0.005 mole of Ia-d or IIa-d in 10-15 ml of nitrobenzenes was refluxed for 6-8 h, after which the reaction mixture was cooled, and the precipitate was removed by filtration and washed with 10-20 ml of ethanol. The compounds were obtained in 88-93% yields. Two crystallizations from nitrobenzene gave quinacridones IIIa, c, d in 63-75% yields. The physicochemical characteristics of the products were in agreement with the literature data [11].

Alternative Syntheses. 3-Bromo-7,8-phthalylacridone, 2-bromo-7,8-phthalylacridone, and 3-methyl-7,8-phthalylacridone were obtained by the reaction of 1-nitroanthraquinone-2-carboxylic acid with, respectively, p-bromoaniline, m-bromoaniline, and p-toluidine [7]. 1-Amino-2-(p-methylbenzyl)anthraquinone was obtained by the reaction of 1-amino-2-(hydroxymethyl)anthraquinone with toluene in the presence of anhydrous aluminum chloride [12].

1-Azido-2-(p-methylbenzyl)anthraquinone (Ie). This compound, with mp 112-113°C, was obtained in 98% yield from the corresponding amine by a method similar to that used to prepare Ia-d. UV spectrum, λ_{max} (log ε): 375 nm (3.64). Found, %: N 12.0. $C_{22}H_{15}N_3O_2$. Calculated, %: N 11.9.

3-(p-Methylbenzyl)anthra[1,9-cd]isoxazol-6-one (IIe). This compound, with mp 162-164°C, was obtained in 87% yield from the corresponding azide by a method similar to that used to prepare IIa-d. UV spectrum, λ_{max} (log ε): 433 (3.78) and 458 nm (3.76). Found, %: N 4.4. $C_{22}H_{15}NO_2$. Calculated, %: N 4.3.

3-(p-Methylbenzoyl)anthra[1,9-cd]isoxazol-6-one (IIb). A 6.5-g sample of selenium dioxide was added with stirring to a solution of 0.65 g (0.002 mole) of IIe in 200 ml of acetic acid, and the mixture was refluxed with stirring for 2 h. It was then cooled and diluted with 200 ml of water, and the precipitate was removed by filtration, washed with water, dried, and crystallized from o-dichlorobenzene to give 0.36 g (54%) of a compound that was identical to IIb according to the data from the PMR, IR, and UV spectra. PMR spectrum (D_2SO_4), δ: 2.7 ppm (s, CH_3).

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RESEARCH IN THE 2,5-DIARYL-1,3,4-OXADIAZOLE SERIES.

1. ELECTRONIC STRUCTURES AND SPECTRAL-LUMINESCENCE PROPERTIES OF SUBSTITUTED 2,5-DIPHENYL-1,3,4-OXADIAZOLES

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The dependence of the spectral-luminescence properties of substituted 2,5-diphenyl-1,3,4-oxadiazoles on the electronic nature of the substituents was studied. Experimental and theoretical studies confirm the electron-acceptor character of the oxadiazole ring and constitute evidence for the rather effective transmission of the electronic effects through the heteroring.

The intense fluorescence and short lifetimes of the excited states of the 2,5-diaryl-substituted 1,3,4-oxadiazoles have been responsible for their use in scintillation technology and as the active media of lasers. The interest in the study of the dependence of the spectral-luminescence properties on the electronic structures of molecules in this series of compounds is linked with this fact. Despite the considerable number of studies devoted to the structures and properties of 2,5-diaryl-1,3,4-oxadiazoles (see reviews [1, 2]), the character of the electronic interactions between the heteroring and the π systems of the aromatic substituents has not been adequately studied. There is no unified opinion regarding the electronic nature of the oxadiazole ring itself in these molecular systems. Thus, in addition to data on the aromatic character of the heteroring [3, 4], there is information that makes it possible to regard it to a great extent as a conjugated diene [5, 6], whereas the results obtained in [7] lead to the conclusion that appreciable interaction of the π systems of the substituents through the heteroring is absent.

Studies of the effect of the substituents with identical and different electronic natures in the para positions of the phenyl rings of 2,5-diphenyl-1,3,4-oxadiazole (PPD) on the spectral-luminescence properties of the compounds (Table 1) are continued in the present paper. The dipole moments in the ground and first excited singlet states were measured for some of them, and quantum-chemical calculations of the absorption spectra and the electron-density distributions were made.

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