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SYNTHESIS AND BASE-CATALYZED RECYCLIZATION OF 3-ARYLAMINO-CARBONYLANTHRA[1,9-cd]-6-ISOXAZOLONES

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Thermolysis of 1-azido-2-arylaminocarbonylanthraquinones in nonpolar solvents leads to 3-arylaminocarbonylanthra[1,9-cd]-6-isozazolones. By the action of bases, these compounds recyclize in aprotic solvents into 2-arylanthra[1,2-d]-1H-pyrazolin-3,6,11-triones.

It was shown in [1-3] that 3-arylanthra[1,9-cd]-6-isoxazolones isomerize on heating to anthraquinone derivatives containing an angularly condensed six-membered heterocyclic ring at the 1,2-positions. The aim of the present work was to search for new derivatives of anthra[1,9-cd]-6-isoxazolone able to undergo similar isomerizations.

3-Arylaminocarbonylanthra[1,9-cd]-6-isoxazolones (IIIa-i) (Table 1) were synthesized by thermolysis of 1-azido-2-arylaminocarbonylanthraquinones (Ia-i) in boiling toluene. The UV spectra of compounds IIa-i are characterized by the presence of an intense absorption in the 460-480 nm region, characteristic of structurally similar 3-aroylanthra[1,9-cd]-6-isoxazolones

TABLE 1. 3-Arylaminocarbonylanthra[1,9-cd]-6-isoxazolones

Compound	Mp, °C	UV spectrum, λ_{max}, nm (log ε)	Found N, %	Empirical formula	Calculated N, %	Yield, %
IIa	206—208	459 (4,20)	8,4	$C_{21}H_{12}N_2O_3$	8,2	84
IIb	218—220	460 (4,22)	6,8	$C_{21}H_{11}BrN_2O_3$	6,7	79
IIc	210—212	460 (4,22)	6,5	$C_{21}H_{11}BrN_2O_3$	6,7	93
IId	217—219	461 (4,18)	7,7	$C_{21}H_{11}ClN_2O_3$	7,5	75
IIe	209—211	459 (4,19)	7,9	$C_{22}H_{14}N_2O_3$	7,9	89
IIf	217—219	459 (4,19)	8,3	$C_{22}H_{14}N_2O_3$	7,9	78
IIg	214—216	460 (4,22)	8,2	$C_{22}H_{14}N_2O_3$	7,9	84
IIh	202—205	459 (4,09)	7,5	$C_{22}H_{14}N_2O_4$	7,6	75
IIi	216—218	460 (4,23)	7,6	$C_{23}H_{16}N_2O_3$	7,6	66

TABLE 2. 2-Arylanthra[1,2-d]-1H-pyrazoline-3,6,11-triones

Compound	Mp, °C	UV spectrum, λ_{max}, nm (log ε)	Found N, %	Empirical formula	Calculated N, %	Yield, %
IIIa	276—278	462 (3,48)	8,4	$C_{21}H_{12}N_2O_3$	8,2	77
IIIb	310—312	462 (3,39)	7,0	$C_{21}H_{11}BrN_2O_3$	6,7	70
IIIc	251—253	462 (3,47)	7,1	$C_{21}H_{11}BrN_2O_3$	6,7	81
IIId	268—270	475 (3,56)	7,2	$C_{21}H_{11}ClN_2O_3$	7,5	80
IIIe	301—303	480 (3,53)	7,9	$C_{22}H_{14}N_2O_3$	7,9	70
IIIf	310—312	462 (3,42)	8,2	$C_{22}H_{14}N_2O_3$	7,9	70
IIIg	278—280	466 (3,51)	8,2	$C_{22}H_{14}N_2O_3$	7,9	86
IIIh	235—238	466 (3,48)	7,8	$C_{22}H_{14}N_2O_4$	7,6	77
IIIi	290—292	482 (3,53)	7,7	$C_{23}H_{16}N_2O_3$	7,6	83

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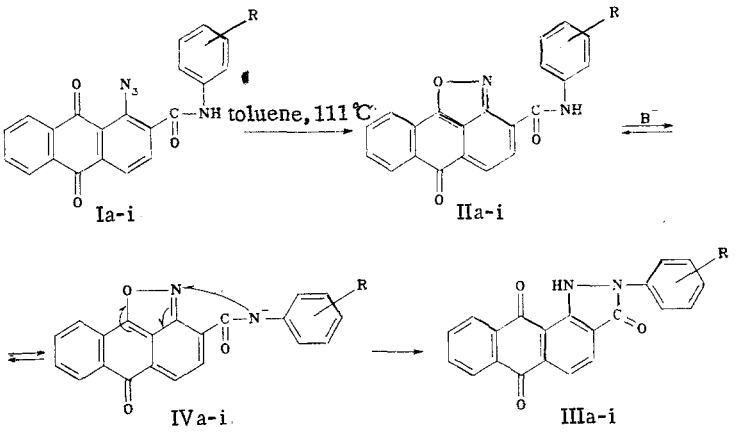
[3]. We found a negative deviation from the Bouguer–Lambert–Beer law for the UV spectra of compounds IIa-i at a concentration higher than $0.7 \cdot 10^{-1}$ mole/liter. In the IR spectra of compounds IIa-i, the stretching vibrations of the NH bond appear in the 3330-3370 cm^{-1} region, and in the 1600-1700 cm^{-1} region there is a group of intense stretching vibrations of the C=O and C=N bonds.

We found that when held at normal temperatures in DMFA in the presence of potassium carbonate, isoxazolones are converted into 2-arylanthra[1,2-d]-1H-pyrazoline-3,6,11-triones (IIIa-i) (Table 2). The recyclizations already described in [1-3] of 3-arylanthra[1,9-cd]-6-isoxazolones into 5,6-phthalylphenothiazines, 5,6-phthalylphenoxazines, and 7,8-phthalylacridones proceed at 120-210°C, which clearly indicates that the O–N bond in the initial isoxazoles must be cleaved at the first stage of the reaction. The formation of pyrazolones IIIa-i under mild conditions in the presence of a basic catalyst shows that the isomerization of II → III proceeds by the "nonnitrene" path. It is probable that the first stage of the recyclization of isoxazolones IIa-i is their ionization at the NH bond.



I—III a R=H; b R=4-Br; c R=3-Br; d R=2-Cl; e R=2-CH_3; f R=3-CH_3; g R=4-CH_3; h R=3-OCH_3; i R=2,5-$(CH_3)_2$

The anion IV formed is further converted by a coordinated mechanism into pyrazolone III. The participation of anion IV in the limiting stage of the reaction is confirmed by the dependence that we obtained in the study of the II → III recyclization kinetics (Fig. 1).

The value of tan α of the slope of the line in Fig. 1 with reference to the abscissa indicates that the monodeprotonated form IVa participates in the slow stage [4].

In the IR spectra of pyrazolones IIIa-i an intense band of stretching vibrations of the NH bond is observed in the 3300-3380 cm^{-1} region, while in the 1690-1700 cm^{-1} region an intense band appears of the vibrations of the C=O group contained in 2H-pyrazolinones [5]. In the UV spectra of these compounds in inert solvents, an absorption band with a maximum at 460-480 nm is observed. In basic solvents, pyrazolones IIIa-i are readily deprotonated, which is accompanied by the disappearance of the absorption at 460-480 nm, increase in the intensity of the absorption at 350 nm, and the appearance of an absorption band with a maximum in the 670-680 nm region.

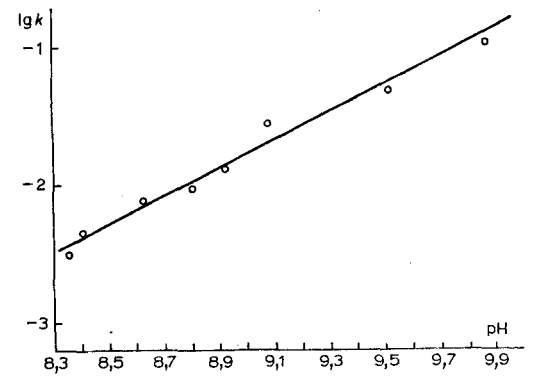
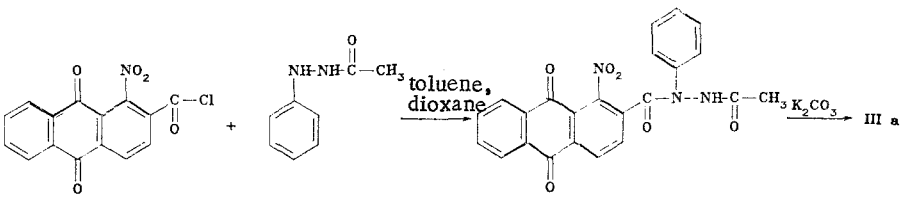


Fig. 1. Dependence of log k_{eff} (sec^{-1}) on pH of recyclization of 3-phenylaminocarbonylanthra-[1,9-cd]-6-isoxazolone (IIa) into 2-phenylanthra[1,2-d]-pyrazoline-3,6,11-trione (IIIa): tg α ≈ 1, r = 0.996; S = 0.006.

The molecular weight and composition of compound IIIa were determined mass-spectrometrically. The same pyrazolone was synthesized by an independent path from 1-nitro-2-chlorocarbonylanthraquinone and α-phenyl-β-acetylhydrazine:



The reaction that we discovered is reminiscent of the isomerizations of isoxazoles described in [6].

a–b–c = CR=N–NH–R; CR=N–OH; NH–CH=NR; NH–CS–NHPh

The recyclization of II → III differs from these examples in that in isoxazolones II fragment *a* is endocyclic. Isomerizations of this type in the series of anthranyls have not yet been sufficiently studied. Due to the availability of anthra[1,9-cd]-6-isoxazolones containing different substituents at the 3-position, the reactivity of anthranyls can be studied more thoroughly.

EXPERIMENTAL

The UV spectra of compounds IIa-i and IIIa-i were run on the SF-14 spectrophotometer, in toluene and DMFA, respectively. The UV spectra of compounds Ic, h and of 1-nitro-2-arylaminocarbonylanthraquinones were run on the UV-vis apparatus in dioxane, and the IR spectra on the Specord 75-IR apparatus in mineral oil. The mass spectra of pyrazolone IIIa was obtained on the MS-902 apparatus from the firm AEI at an energy of the ionizing electrons of 70 eV and at a temperature of direct introduction into the system of 180-200°C. The melting points of pyrazolones IIIa-i and 1-nitro-2-arylaminocarbonylanthraquinones were measured on the PTP-1 apparatus, and those of the remaining compounds on the Boetius microheater stage. The course of the reaction and the purity of the compounds were controlled by TLC on Silufol plates (acetone–toluene, 1:5).

1-Azido-2-arylaminocarbonylanthraquinones were obtained from 1-nitro-2-arylaminocarbonylanthraquinones (V) by the method described in [7].

1-Nitro-2-arylaminocarbonylanthraquinones (see Table 3). A 0.02-mole portion (6.3 g) of 1-nitro-2-chlorocarbonylanthraquinone is added to a solution containing 0.04 mole of the arylamine in 100 ml of dioxane. The mixture is stirred for 2 h at 20-25°C and then diluted with water, and the products are filtered and crystallized from o-dichlorobenzene.

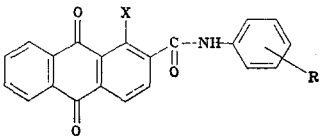
The physical constants of azides Ic, h and 1-nitro-2-arylaminocarbonylanthraquinones (Vc, h) not yet described are listed in Table 3.

3-Arylaminocarbonylanthra[1,9-cd]-6-isoxazolones (II). A solution of 0.005 mole of azides Ia-i in 50-100 ml of toluene is boiled for 3-6 h. After cooling to 20-25°C, the isoxazolones IIa-i are filtered, and crystallized from toluene.

2-Arylanthra[1,2-d]-1H-pyrazoline-3,6-11-triones (IIIa-i). A solution of 0.01 mole of isoxazoles IIa-i in 100 ml of dimethylformamide is stirred for 3-6 h at 20-25°C in the presence of 1.2 g of potassium carbonate. The mixture acquires a green color. It is then acidified by 5 ml of acetic acid and diluted with water to 300-500 ml. The pyrazolines IIIa-i are filtered and purified by recrystallization from o-dichlorobenzene.

Independent Synthesis of Pyrazolone IIIa. 1-Nitro-2-chloro-carbonylanthraquinone, 3.16 g (0.01 mole), is added to a suspension of 2.25 g (0.015 mole) of α-phenyl-β-acetylhydrazine in 150 ml of dry toluene. The mixture is heated with stirring to 40°C and held at these conditions for 30 min. It is then cooled to 20-25°C and held for another 40 h. The precipitate is filtered and washed with 20 ml of ethanol and 40 ml of ether. Yield 3.67 g (86%) of 1-nitro-2-(α-acetyl-β-phenylhydrazino)carbonylanthraquinone (VI), mp 250-252°C. IR spectrum: 3315 (NH); 1705, 1680 cm^{-1} (C=O). Found, %: N 9.6. $C_{23}H_{15}N_3O_6$. Calculated, %: N 9.8.

TABLE 3. 1-Nitro-2-arylaminocarbonylanthraquinones and 1-Azido-2-arylaminocarbonylanthraquinones



Compound	X	R	Mp, °C	UV spectra, λ_{max}, nm (log ε)	Found N, %	Empirical formula	Calculated N, %	Yield, %
Ic	N_3	*m*-Br	196—198	327 (3,81)	13,2	$C_{21}H_{11}BrN_4O_3$	12,5	98
Ih	N_3	*m*-OCH_3	194—196	327 (3,89)	13,3	$C_{22}H_{14}N_4O_4$	14,0	98
Vc	NO_2	*m*-Br	318—320	363 (3,73)	5,8	$C_{21}H_{11}BrN_2O_5$	6,2	97
Vh	NO_2	*m*-OCH_3	248—250	367 (3,72)	6,7	$C_{22}H_{14}N_2O_6$	6,9	87

A solution of 2.15 g (0.005 mole) of compound VI in 60 ml of DMFA is stirred for 70 h in the presence of 1 g of K_2CO_3. The reaction mixture is acidified with 5-10 ml of acetic acid, diluted with water to 300 ml, and filtered. The precipitate is held for 3-4 h in 30 ml of 80% H_2SO_4 at 40-50°C, and after filtration, poured on 100-150 g of ice to yield a compound identical with IIIa, in a yield of 67%. Found, %: N 7.8. $C_{21}H_{12}N_2O_3$. Calculated, %: N 8.2.

Kinetic Measurements. The buffer solutions (pH 8.35-9.80) are prepared by mixing the corresponding amounts [8] of 0.2 mole of aqueous solutions of NaOH and KH_2PO_4, bringing their volume up to 57 ml, and then adding freshly distilled DMFA. The IIa → IIIa recyclization kinetics is studied spectrophotometrically in a thermostated block of the Specord UV-vis apparatus at 35°C, in cuvettes 1 cm thick. The solution of isoxazole IIa (0.21 ml) in dioxane is introduced into 25 ml of a thermostated buffer solution, while the concentration of compound IIa is $0.5 \cdot 10^{-4}$ mole/liter. The solution obtained is transferred into a cuvette, and the optical density is measured at given periods of time at 345 nm, where the deprotonated form of pyrazolone IIIa is absorbing. The rate constants of a first-order reaction and the correlation of log k_{ef} with pH are calculated by the usual method.

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