REACTIONS OF 3(5)-HALO-6-OXO-6H-ANTHRA[1,9-*cd*]ISOXAZOLES WITH ARENETHIOLS

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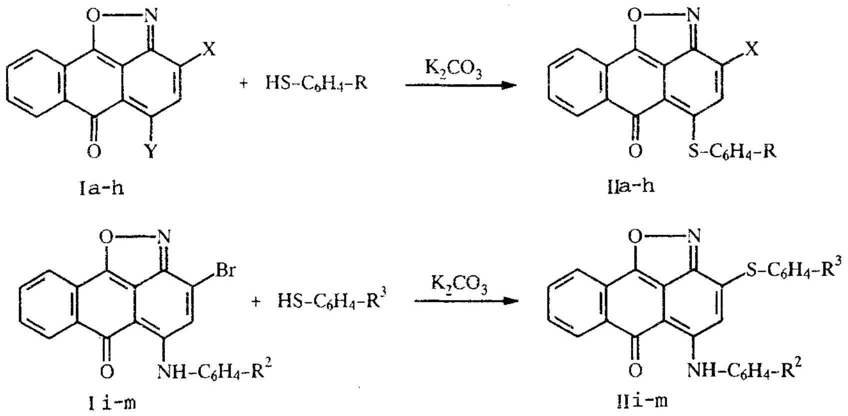
The corresponding 3(5)-arylthio-6-oxo-6H-anthra[1,9-cd]isoxazoles are formed as a result of the reaction of 3(5)-halo-6-oxo-6H-anthra[1,9-cd]isoxazoles with arenethiols.

It has been previously shown [1-3] that 6-oxo-6H-anthra[1,9-*cd*]isoxazoles I, which contain halogen atoms in the 5 and/or 3 positions, undergo nucleophilic substitution of the halogens under the influence of N-, C-, and O-nucleophiles; depending on the reaction conditions and the nucleophilicity of the reactant, substitution took place both in the 5 position and in the 3 position of the substrates (Ia-h).

The reactions of isoxazoles Ia-m with S-nucleophiles have not been previously studied, although their possible products, viz., 3-arylthio-6-oxo-6H-anthra[1,9-*cd*]isoxazoles II, may serve as starting substances for the synthesis of naphtho[2,3-*a*]phenothiazine-8,13-diones IIIa-e, which are of practical importance [4, 5].

We have found that isoxazoles Ia-m react quite readily with thiophenols in dioxane in the presence of potassium carbonate at 25-60°C (Table 1). Replacement of the halogen atom in the 5 position took place at a lower temperature than replacement in the 3 position; this is in agreement with our previously obtained experimental data and quantum-chemical calculations [6] with respect to the greater electrophilicity of the 5 position.



Ia-e X = H, Y = Cl; b,f X = Y = Br; c,g X = Y = Cl; d,h X = CH_3, Y = Br; IIa X = H, R = H; h X = Br, R = H; c X = Cl, R = H; d X = CH_3, R = H; e X = H, R = CH_3; f X = Br, R = CH_3; g X = Cl, R = CH_3; h X = CH_3, R = CH_3; I—IIi R^2 = H; I—II j-m R^2 = CH_3; IIj R^3 = H; IIk R^3 = NO_2; IIm R^3 = OCH_3;
IIi,l R^3 = CH_3

The site of incorporation of one arylthio group into substrates Ib, c was confirmed by the reduction of IIb, c, respectively, to give 1-amino-4-phenylthio-9,10-anthraquinone (λ_{max} = 524 nm) and 1-amino-2-bromo-4-phenylthio-9,10-anthraquinone (λ_{max} = 531 nm). 1-Amino-2-phenylthio-9,10-anthraquinone, which we obtained independently, is characterized by a long-wave maximum only at 481 nm. This effect of electron-donor substituents in the 2 and 4 positions of 1-amino-9,10-anthraquinone on the location of the absorption bands in the UV spectra is in agreement with the literature data [7].

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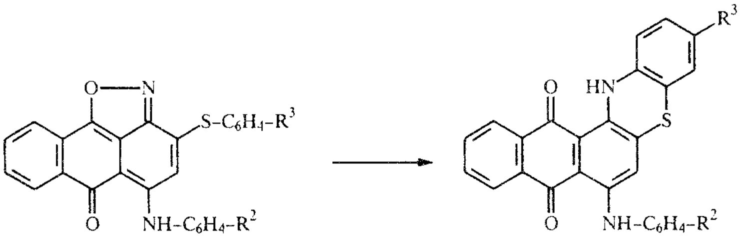
TABLE 1. Characteristics of the Synthesized IIa-m

Compound	Empirical formula	mp, °C	UV spectra, λ_{max}, nm (lg ε)	Yield, %
IIa	$C_{20}H_{11}NO_2S$	187...189	351 (3,94); 374 (3,90); 464 (4,18); 495 (4,31)	84
IIb	$C_{20}H_{10}BrNO_2S$	263...265	360 (3,90); 378 (3,90); 471 (4,19); 502 (4,34)	85
IIc	$C_{20}H_{10}ClNO_2S$	264...266	358 (3,90); 375 (3,90); 468 (4,18); 498 (4,32)	83
IId	$C_{21}H_{13}NO_2S$	217...219	355 (3,90); 373 (3,83); 462 (4,12); 491 (4,25)	92
IIe	$C_{21}H_{13}NO_2S$	200...202	357 (3,89); 373 (3,90); 467 (4,21); 495 (4,28)	81
IIf	$C_{21}H_{12}BrNO_2S$	264...266	359 (3,86); 377 (3,92); 471 (4,20); 500 (4,37)	82
IIg	$C_{21}H_{12}ClNO_2S$	260...262	358 (3,81); 377 (3,89); 470 (4,13); 500 (4,27)	80
IIh	$C_{22}H_{15}NO_2S$	117...119	356 (3,86); 373 (3,80); 463 (3,74); 493 (4,24)	90
IIi	$C_{27}H_{18}N_2O_2S$	206...207	360 (4,03); 385 (4,02); 505 (4,32); 532 (4,39)	71
IIj	$C_{27}H_{18}N_2O_2S$	174...175	360 (3,94); 383 (3,94); 508 (4,25); 535 (4,27)	82
IIk	$C_{27}H_{17}N_3O_4S$	225...226	360 (3,98); 376 (3,95); 505 (4,18); 532 (4,25)	83
IIl	$C_{28}H_{20}N_2O_2S$	220...221	361 (3,98); 383 (3,99); 505 (4,30); 532 (4,34)	85
IIm	$C_{28}H_{20}N_2O_3S$	215....216	361 (4,01); 383 (4,01): 505 (4,33); 535 (4,37)	86

7-Hydroxynaphtho[2,3-*a*]phenothiazine-8,13-diones III are promising as IR dyes [8] because of the presence of an absorption maximum at 700 nm. In this connection, it seemed of interest to synthesize 7-arylaminonaphtho[2,3-*a*]phenothiazine-8,13-diones III from the isoxazoles IIi-m that we obtained.

When isoxazolones IIi-m were refluxed in nitrobenzene, they did, in fact, undergo isomerization to azines III, which were obtained in high yields. Their long-wave absorption maxima are also found at 700 nm; this indicates the possibility of their practical utilization (Table 2).



IIi-m IIIa-e

IIi IIIa R^2 = H; IIj-m IIIb–e R^2 = CH_3; IIi-l IIIa,d R^3 = CH_3; IIj,IIIb R^3 = H;
IIk IIIc R^3 = NO_2; IIm, IIIe R^3 = OCH_3

EXPERIMENTAL

The IR spectra 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 melting points were determined on a Boëtius heating platform.

The results of analysis of the synthesized compounds for N, S, and Hal were in agreement with the calculated values.

Arylthio-6-oxo-6H-anthra[1,9-*cd*]isoxazoles IIa-m (General Method). A 3.6-mmole sample of potassium carbonate and 2 mmole of the thiophenol were added to a solution of 2 mmole of starting isoxazole Ia-m in 30-50 ml of dry dioxane, and the mixture was stirred for 4-8 h at 20-25°C. The solution was then poured into 500 ml of ice water, and the precipitated IIa-m were removed by filtration, washed with water, and dried.

1-Amino-2-bromo-4-phenylthio-9,10-anthraquinone. A mixture of 0.2 g (0.5 mmole) of isoxazole IIb and 0.1 g of a catalyst (Pd/C) in 150 ml of dioxane was hydrogenated with hydrogen at 50°C and atmospheric pressure until hydrogen absorption ceased (~3 h). The catalyst was removed by filtration, the solution was evaporated, and the precipitated 1-amino-2-bromo-4-phenylthio-9,10-anthraquinone was removed by filtration. The yield of the product, which had mp 228-230°C (from ethanol), was 0.12 g (60%).

1-Amino-4-phenylthio-9,10-anthraquinone was similarly obtained.

TABLE 2. Characteristics of the Synthesized IIIa-e

Compound	Empirical formula	mp, °C	UV spectra, λ_{max}, nm (lg ε)	Yield, %
IIIa	$C_{27}H_{18}N_2O_2$	256...257	447 (3,7); 600 (3,9); 645 (4,1); 704 (4,2)	92
IIIb	$C_{27}H_{18}N_2O_2$	286...288	446 (3,71); 592 (3,91); 641 (4,21); 694 (4,21)	70
IIIc	$C_{27}H_{17}N_3O_4$	348...349	467 (3,71); 595 (3,81); 630 (4,1); 6,80 (4,1)	90
IIId	$C_{28}H_{20}N_2O_2$	280...281	450 (3,71); 599 (3,91); 649 (4,21); 704 (4,21)	95
IIIe	$C_{28}H_{20}N_2O_2$	234...235	450 (3,75); 606 (3,94); 658 (4,22); 714 (4,21)	97

7-Hydroxynaphtho[2,3-*a*]phenothiazine-8,13-diones IIIa-e (General Method). A 0.8-mmole sample of IIi-m was refluxed in 8 ml of nitrobenzene for 20-60 min, after which the mixture was cooled, and the precipitated IIIa-e were removed by filtration and recrystallized from o-dichlorobenzene.

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