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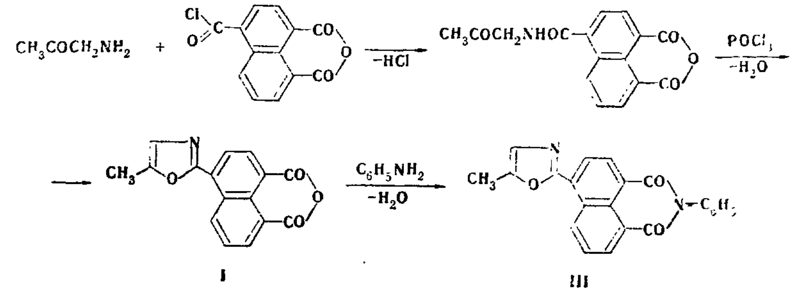
4-(5-METHOXY-2-OXAZOLYL)NAPHTHALIC ANHYDRIDE AND PRODUCTS OF ITS CONDENSATION WITH AROMATIC AMINES

B. M. Krasovitskii and V. M. Shershukov

UDC 547.787.3'836.7'785.5:
542.953:543.422.6

4-(5-Methyl-2-oxoazolyl)naphthalic anhydride was synthesized by condensation of 4-chloroformylnaphthalic anhydride with aminoacetone and subsequent cyclization of the resulting amide. Luminescing methyl-substituted N-phenylnaphthalimide and 1,8-naphthoylene-1',2'-benzimidazole were obtained by condensation of this product with aniline and o-phenylenediamine, respectively. The relationship between the structures of the products and their electronic absorption and luminescence spectra was investigated.

We have previously described 2,5-diaryl-substituted oxazoles with a peri-anhydride grouping that makes it possible to obtain organic luminophores with luminescences of various colors [1, 2]. In a continuation of our research we synthesized 4-(5-methyl-2-oxazolyl)naphthalic anhydride (I) by condensation of 4-chloroformylnaphthalic anhydride [3] with aminoacetone [4] and subsequent dehydration of the resulting amide.



Shortening of the conjugation chain in I as compared with 4-(5-phenyl-2-oxazolyl)naphthalic anhydride (II) [2] gives rise to a hypsochromic effect in the absorption and a hypsofluoric effect in the luminescence (Table 1). It is remarkable that the absolute photoluminescence quantum yield (η) in toluene increases. This is especially interesting since 2-(1-naphthyl)-5-methyloxazole, in contrast to 2-(1-naphthyl)-5-phenyloxazole, which luminescences intensely in toluene, has only weak luminescence [5]. The luminescence properties of I are possibly due to a considerable extent to donor–acceptor interaction, although weak, of the methyl group and the anhydride grouping.

Phenylimide III, which differs little from the starting anhydride with respect to its spectral-luminescence characteristics but is sensitive to a change in the pH of the medium, was obtained by heating methyloxazolylnaphthalic anhydride with aniline.

The formation of a mixture of isomeric 4- and 5-substituted 1,8-naphthoylene-1',2'-benzimidazoles (IV and V) is possible in the reaction of oxazolylnaphthalic anhydride with o-phenylenediamine. Unsubstituted

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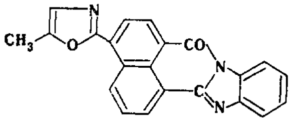
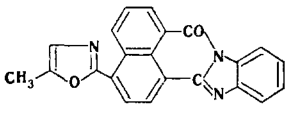
TABLE 1. Electronic Absorption Spectra and Luminescence Properties of the Compounds Obtained

Compound	Absorption		Luminescence	
	λ_{max} in toluene, nm	$\varepsilon \cdot 10^{-4}$	λ_{max} in toluene, nm	η
I	375	1,89	440	0,29
II [2]	295	1,06	480	0,23
	398	2,20		
III	375	2,50	440	0,22
IV–V	300	1,72	515	0,36
	422	2,72		
VI [6]	388	1,20	490	0,55

naphthoylenebenzimidazole (VI) is known to be an effective luminophore with yellow-green luminescence and has found various applications [6].


IV


V

Since 4- and 5-phenyloxazolyl-substituted naphthoylenebenzimidazoles [7] differ little with respect to their spectral-luminescence properties, we, having obtained the product of condensation of methyloxazolylnaphthalic anhydride with o-phenylenediamine (a mixture of IV and V), investigated it without isolating the isomers. The introduction of a methyloxazolyl group in the naphtholyenebenzimidazole molecule shifts the absorption and luminescence considerably to the long-wavelength region, but the absolute photoluminescence quantum yield decreases.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds were measured with an SF-4A spectrophotometer, and the luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 emission pickup, 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 quartz monochromator. The absolute luminescence quantum yields were determined by the equal absorption method [8]. "Especially pure" toluene was used as the solvent.

4-(5-Methyl-2-oxazolyl)naphthalic Anhydride (I). A mixture of 15 g of 4-chloroformylnaphthalic anhydride in 200 ml of benzene and 5.5 g of aminoacetone hydrochloride in 300 ml of water was stirred vigorously and made alkaline with 10% NaOH, and the resulting precipitate was removed by filtration, washed with water, dried, and refluxed with 50 ml of phosphorus oxychloride for 2 h. The resulting solution was poured over 200 g of ice, and the precipitate was removed by filtration, washed with water, and dried to give 12 g (81%) of a product with mp 268° (from acetic anhydride). Found: C 68.5; H 3.1; N 4.8%. $C_{16}H_9NO_3$. Calculated: C 68.8; H 3.2; N 5.0%.

4-(5-Methyl-2-oxazolyl)naphthalic Acid N-Phenylimide (III). A 1.4-g (1.5 mmole) sample of freshly distilled aniline was added to a refluxing solution of 3 g (0.1 mmole) of 4-(5-methyl-2-oxazolyl)naphthalic anhydride in 50 ml of glacial acetic acid, after which the mixture was refluxed for 4 h and poured into 100 ml of water. The resulting precipitate was removed by filtration, washed successively with 5% HCl, water, 5% $NaHCO_3$, and water to neutrality, and dried to give 3.5 g (99%) of III. Crystallization from xylene and chromatographic purification of a benzene solution of the product on aluminum oxide gave a product with mp 204-205°. Found: C 74.2; H 4.0; N 8.2%. $C_{22}H_{14}N_2O_3$. Calculated: C 74.5; H 4.0; N 7.9%.

4(5)-(5-Methyl-2-oxazolyl)-1,8-naphthoylene-1',2'-benzimidazole (IV-V). A mixture of 2.8 g of 4-(5-methyl-2-oxazolyl)naphthalic anhydride and a 1.5-fold excess (1.6 g) of o-phenylenediamine was refluxed in 50 ml of glacial acetic acid for 4 h, after which it was cooled, and the resulting precipitate was removed by filtration, washed successively with 5% HCl, water, 5% $NaHCO_3$, and water, and dried to give 3.4 g (97%) of product. Crystallization from xylene and chromatographic purification of a benzene solution of the product on aluminum oxide gave a product with mp 243-244°. Found: C 75.0; H 3.4; N 11.8%. $C_{22}H_{13}N_3O_2$. Calculated: C 75.2; H 3.7; N 12.0%.

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CYCLIZATION OF o-NITROSOACYLBENZENES TO ANTHRANILS

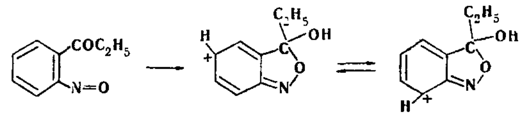
S. S. Mochalov, T. P. Surikova,
and Yu. S. Shabarov

UDC 547.786.3.07

5-Bromo- and 5-methoxy-3-ethylanthranils, respectively, were obtained by cyclization of o-nitrosopropiophenone under the influence of hydrogen bromide in benzene and hydrogen chloride in methanol. In these reactions, the starting nitroso ketone undergoes redox transformations that also proceed readily in an inert solvent in the absence of any cyclizing reagents.

There have been previous reports of the synthesis of various anthranils by cyclization of substituted o-nitrosoacylbenzenes under the influence of zinc in glacial acetic acid [1], triphenylphosphine [2], and dry hydrogen chloride in benzene [3]. It was noted that in the latter case the introduction of a halogen atom in the 5 or 7 position of the resulting anthranilic system is always observed.

In [3] it was assumed that the conversion to an anthranil proceeds through a step involving the formation of benzenonium ions of the A and B type:



I A B

The latter on adding a nucleophile (chloride ion) gave hexadiene chloro derivatives, which were converted to the corresponding anthranils under the reaction conditions.

Using hydrogen bromide in benzene and hydrogen chloride in methanol as the cyclizing agents we hoped, first of all, to show the general character of this method for the synthesis of substituted anthranils, and, second, to obtain additional proof for a process occurring via the pathway proposed above.

M. V. Lomonosov Moscow State University, N. I. Pirogov Moscow State Medical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 886-890, July, 1976. Original article submitted June 10, 1975.