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SUBSTITUTED 2-ARYLIMINONAPHTHO[1,8-bc]THIOPHENE

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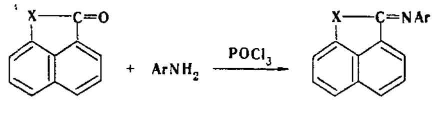
UDC 547.732.734.736.07:668.8

The first dyes based on naphtho[1,8-bc]thiophen-3-(2H)-one were synthesized. The carbonyl group of these compounds has lower reactivity than the carbonyl group of naphthostyryl in condensation with arylamines.

Naphtho[1,8-bc]thiophen-3(2H)-one (I) is isoelectronic with respect to naphthostyryl (II) and 1-phenalenone. Approximately 100 patents on dyes from naphthostyryl have been granted in the last 15 years. On the other hand, although the methods for the preparation of and the physical and chemical properties of I have been studied (for example, see [1-3]), not one specific dye based on it has been described.

We have synthesized yellow disperse dyes of the general formula IV (see Table 1) that include a naphtho[1,8-bc]thiophene fragment by condensation of naphthothiophenone I with aromatic amines III, containing a nitro group, in the presence of phosphorus oxychloride.

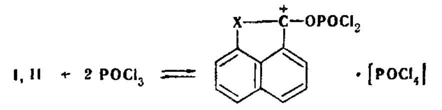


I, II III IVa-f, V

IVa-f, I X=S; II, V X=NH

The dyes on lavsan have good light fastness but unsatisfactory resistance to sublimation at 200° (Table 1).

In contrast to naphthostyryl [4], I does not give Schiff bases (V) with aniline and other amines that do not contain a nitro group (o-bromoaniline, aminoacenaphthene, p-aminobenzoic acid, etc.). The mechanism of the condensation of carbonyl-containing substances with amines in the presence of phosphorus oxychloride has usually not been considered [5, 6].



(1)

VI X=S; VII X=NH

$$ArNH_2 + 2\,POCl_3 \rightleftharpoons (ArNH_2 \cdot \overset{+}{POCl_2}) \cdot POCl_4^- \quad (2)$$

$$VI, VII + ArNH_2 \longrightarrow IV, V + HPOCl_4 + PO(OH)Cl_2 \quad (3)$$

If phosphorus oxychloride is capable (see [7]) of undergoing reactions (1) and (2), it may be assumed (see [8]) that nitroanilines, retaining sufficient nucleophilicity for reaction (3) with carbonium ion VI, have relatively low basicities that insure the presence in solution of the necessary concentration of the free amine, not deactivated by reaction with phosphorus oxychloride. Basic amines (aniline, etc.) react with phosphorus oxychloride

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Rubezhnoe Branch of the Scientific-Research Institute of Intermediates and Dyes. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1036-1038, August, 1976. Original article submitted July 15, 1975; revision submitted January 27, 1976.

TABLE 1. Characteristics of Substances of the General Formula IV

Compound	Ar	mp, °C (from benzene)	Empirical formula	Element	Found, %	Calc., %	λ_{max}, nm	$\varepsilon_{max} \times 10^{-4}$	Fastness indexes on lavsan*					Yield, %
									to hot water	to soap	to sublimation		to light	
											180°30″	200° 30″		
IVa	4-$NO_2C_6H_4$	207	$C_{17}H_{10}N_2O_2$	C H N	66,8 3,1 9,2	66,6 3,3 9,1	392	1,59	5/3—2/3—2/3	5/3—2/3—2/3	5/2/2	5/1/1	7	77,5
IVb	4-NO_2-2-CNC_6H_3	207—209	$C_{18}H_9N_3O_2$	C H N	65,3 2,6 12,1	65,2 2,6 12,6	390	1,48	5/3/3/4	5/3/3/4	5/3/3	5/2/2	6—7	64
IVc	4-NO_2-2-ClC_6H_3	185—186	$C_{17}H_9ClN_2O$	C H N	59,8 2,6 8,0	59,9 2,6 8,2	385	1,34	5/4—5/4/4—5	5/4/4—5/4—5	5/3/3	5/2/2	7	75
IVd	4-NO_2-2-$CH_3C_6H_3$	204—206	$C_{18}H_{12}N_2O_2$	N	8,7	8,7	380	1,01	5/5/4/5	5/5/5/5	5/3/4	5/2/4	6	87
IVe	4-NO_2-2,6-$Cl_2C_6H_2$	238—240	$C_{17}H_8Cl_2N_2O_2$	C H	54,2 2,0	54,1 2,1	378	1,25	—†	—	—	—	—	96
IVf	2,4-$(NO_2)_2C_6H_3$	203	$C_{17}H_9N_3O_4$	C H	58,5 2,5	58,2 2,6	392	1,38	—†	—	—	—	—	64

*In accordance with GOST 97-33-61.

†These dyes are not taken up by lavsan.

more nearly completely. The residual amine concentration is sufficient for reaction with cation VII but inadequate for reaction with cation VI. The high reactivity of cation VII is probably associated with the lower polarizability of the nitrogen atom as compared with the polarizability of the sulfur atom.

The synthesized substances do not luminesce either in solution or in the solid state.

EXPERIMENTAL

The UV spectra of dioxane (purified by the method in [9]) solutions of the compounds were measured with an SF-4A spectrophotometer.

2-(4-Nitrophenylimino)naphtho[1,8-bc]thiophene. A mixture of 1 g (5.3 mmole) of naphtho[1,8-bc]thiophen-2-one, 0.82 g (5.9 mmole) of p-nitroaniline, and 6 ml of chlorobenzene was stirred and heated to 80°, and 0.98 ml (10.6 mmole) of phosphorus oxychloride was added in the course of 30 min. The mixture was then heated at 128° for 4 h, cooled to 20°, and poured into 100 ml of ice water. The aqueous mixture was neutralized to pH 9 with 10% alkali solution, the chlorobenzene was removed by steam distillation, and the resulting precipitate was removed by filtration, washed to neutrality with water, and dried to give yellow needles with mp 207° (from benzene).

The other dyes (see Table 1) were similarly obtained. They were unstable with respect to the action of acids.

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