ABSORPTION SPECTRA OF 3-OXO-2,3-DIHYDROTHIONAPHTHENE AND ITS DERIVATIVES

XVII.* DYES FROM 7-IODO-2H-NAPHTHO[1,8-bc]THIOPYRAN-3-ONE

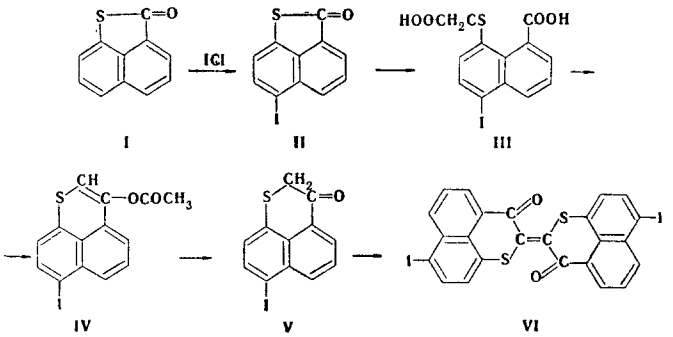
M. A. Mostoslavskii, S. I. Saenko, and V. L. Belyaev

UDC 668.8:547.818.5:543.422.6

Conditions have been found for the iodination of naphtho[1,8-bc]thiophen-2-one. A number of new thioindigoid dyes have been synthesized and their photochemical isomerization has been performed in benzene.

We have previously [2] described the chlorination and bromination of naphtho[1,8-bc]thiophen-2-one (I) with elementary halogens. The iodination of (I) with metallic iodine does not take place. The reaction of iodine chloride under severe conditions forms 6-iodonaphtho[1,8-bc]thiophen-2-one (II) contaminated with a small amount of 6-chloronaphtho[1,8-bc]thiophen-2-one, which is readily separated by a single recrystallization.

The synthesis of (III-VI) (Table 1) takes place smoothly under the conditions found for the corresponding bromine derivatives [2, 3].



The condensation of (V) with the p-dimethylaminoanils of substituted thionaphthene quinones gave a number of unsymmetrical dyes (VII-XIV) (Table 2), solutions of which in benzene were subjected to photochemical trans → cis and cis → trans isomerization. The introduction of an iodine atom into the molecule of the perinaphththioindigo (dye VI) and into the molecules of the dyes (VII-XIV) (Table 2) affects the absorption spectra of the trans and cis forms in just the same way as the introduction of chlorine or bromine [3]. The iodine-substituted dyes were found to have an increased capacity for photochemical trans–cis isomerization.

EXPERIMENTAL

A solution of iodine chloride in acetic acid was prepared as described previously [5]. The concentration of ICl was 900 g/liter.

*For Communication XVI, see [1].

Rubezhnoe Branch of the Scientific-Research Institute of Organic Intermediates and Dyes, Rubezhnoe.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1034-1036, August, 1973. Original article submitted January 31, 1972.

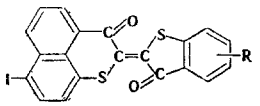
TABLE 1. Properties of Substances (II-VI)

Comp.	Empirical formula	mp, °C	I, % found	I, % calc.	Yield, %
II	$C_{11}H_5IOS$	201—202	40,53	40,65	34,4
III	$C_{12}H_9IO_4S$	238—239	32,63	32,69	98
IV	$C_{14}H_9IO_2S$	116—117	34,22	34,46	85,1
V	$C_{12}H_7IOS$	131—133	38,87	38,90	72,3
VI	$C_{24}H_{10}I_2O_2S_2$*	†	39,00	39,15	55,8

*For the dye (VI) in trichlorobenzene, λ_{max} of the trans form is 652.5 nm (ε_{max} 3.4 · 10^4), and λ_{max} for the cis form 520.5 nm (ε_{max} 2.0 · 10^4).

† The dye undergoes no change up to 300°C, and on further heating it is impossible to determine a distinct melting or decomposition point.

TABLE 2. Properties of the Dyes



(A)

Comp.	R	Empirical formula	Found, % C	Found, % H
VII	6-OC_2H_5	$C_{22}H_{13}IO_3S_2$	51,11	2,44
VIII	4-CH_3, 6-Cl	$C_{21}H_{10}ClIO_2S_2$	48,61	2,24
IX	6-Cl	$C_{20}H_8ClIO_2S_2$	47,20	1,45
X	H	$C_{20}H_9IO_2S_2$	50,66	1,82
XI	5-NO_2	$C_{20}H_8NIO_4S_2$	46,30	1,83
XII	4,5- Benzo	$C_{24}H_{11}IO_2S_2$	54,91	2,09
XIII	6,7-(1′-Cl)- Benzo	$C_{24}H_{10}ClIO_2S_2$	52,07	1,57
XIV	5,6-Benzo, 7-Cl	$C_{24}H_{10}ClIO_2S_2$	51,65	1,66

Comp.	Calc., % C	Calc., % H	trans form λ_{max}, nm	trans form $\varepsilon \cdot 10^4$	cis form λ_{max}, nm	cis form $\varepsilon \cdot 10^4$	Δλ*, nm trans form	Δλ*, nm cis form	Yield, %
VII	51,17	2,53	589	3,3	471,5	1,6	7	1,5	29
VIII	48,43	1,93	597,5	3,7	485	1,8	6,5	6	33
IX	47,40	1,59	598,5	3,3	486,5	1,7	8,5	6,5	37
X	50,85	1,92	600	3,0	487,5	1,6	8	5,5	43
XI	46,43	1,55	603,5	4,0	494,5	2,2	9,5	8,5	40
XII	55,18	2,12	606	3,4	491	1,6	6	4	63
XIII	51,76	1,81	618	2,8	506,5	1,4	9	2,5	64
XIV	51,76	1,81	621	3,3	511	1,7	9	4	53

*Δλ is the difference between λ_{max} of the dye of formula A and the unsubstituted dye [4].

6-Iodonaphtho[1,8-bc]thiophen-2-one (II). Over 30 min, 30 ml of a boiling solution of iodine chloride (27 g, 166 mmoles) in acetic acid was added to 5 g (26.8 mmoles) of naphtho[1,8-bc]thiophen-2-one and the resulting mixture was boiled with 400 ml of water, after which 148 ml of a 27.5% solution of sodium bisulfite was added. After stirring, the precipitate was filtered off, washed with water, and dried. Yield 5.4 g (64.4%), mp 171-176°C. After a single recrystallization from ethanol, mp 198-199°C. For the chemically pure product, mp 201-202°C.

The substances given in Tables 1 and 2 were obtained by methods described previously [2,3].

LITERATURE CITED

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