CONDENSATION OF 5-BROMO-, 3-BROMO-, AND 3-IODOACENAPHTHENEQUINONES WITH 3-HYDROXYTHIONAPHTHENE AND ITS DERIVATIVES

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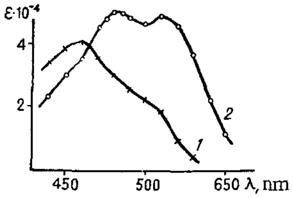
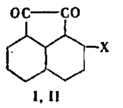
The oxidation of 3-bromo- and 3-iodoacenaphthene has given 3-bromo- and 3-iodoacenaphthenequinones. The condensation of 5-bromo-, 3-bromo-, and 3-iodoacenaphthenequinones with 3-hydroxythionaphthene and its derivatives has yielded indigoid dyes, and the main light absorption maxima of these dyes have been determined.

In a prevous paper [1], we described 3-fluoro- and 3-chloroacenaphthenequinones and also indigoid dyes obtained from them. Continuing our investigation of halogen derivatives of acenaphthenequinones [2], we have synthesized 3-bromo- and 3-iodoacenaphthenequinones and 2-iodonaphthalic anhydride by the oxidation of 3-bromo- and 3-iodoacenaphthenes.

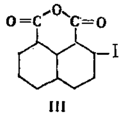


Absorption spectra of the dyes: 1) **X**; 2) **IV**.

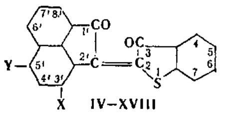
By the condensation of 5-bromo-, 3-bromo-, and 3-iodoacenaphthenequinones with equimolecular amounts of 3-hydroxythionaphthene and its derivatives, and also with indoxyl, indigoid dyes have been obtained in good yields. The properties of the dyes obtained are given in the table.



I, II
I X = Br; II X = I

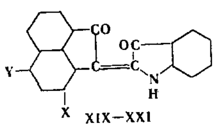


III



IV–XVIII

IV X = Br, Y = H; V X = H, Y = Br; VI X = Br, Y = H, 6-Cl; VII X = H, Y = Br, 6-Cl; VIII X = Br, Y = H, 4-CH_3, 6-Cl; IX X = H, Y = Br, 4-CH_3, 6-Cl; X X = Br, Y = H, 6-OC_2H_5; XI X = H, Y = Br, 6-OC_2H_5; XII X = Br, Y = H, 4,5-benzo; XIII X = H, Y = Br, 4,5-benzo; XIV–XVIII Y = H; XIV X = I; XV X = I, 6-Cl; XVI X = Y, 4-CH_3, 6-Cl; XVII X = I, 6-OC_2H_5; XVIII X = I, 4,5-benzo.



XIX–XXI

XIX X = Br, Y = H; XX X = H, Y = Br; XXI X = I, Y = H.

The absorption spectra of these dyes in the UV and visible regions in chlorobenzene solution have three well-defined maxima. In compounds IV-XI, XIV-XVII, and XIX-XXI, the first maxima are in the UV region between 300 and 310 nm, and in compounds XII, XIII, and XIV they are at 332–335 nm. The second maxima in compounds X-XIII and XVII-XXI are in the UV region between 363 and 405 nm while in compounds IV-IX and XIV-XVI they are in the visible region between 476 and 485 nm. The third maxima in compounds X-XIII, XVII and XVIII are in the visible region between 442 and 463 nm and in compounds IV-IX, XIV-XVI, and XIX-XXI in the long-wave region between 505 and 555 nm.

The replacement by bromine or iodine of the hydrogen atom in position 6 of 3'- and 5'-bromo(iodo) derivatives of 2-(1'-oxoacenaphthylidene)-3-thionaphthenone causes a slight hypsochromic shift, while the replacement of hydrogen in the same position by an ethoxy group gives a hypsochromic shift of from 14 to 22 nm (figure).

As compared with the 3'-bromo derivatives, the 5'-bromo derivatives have a bathochromic shift of 1–11 nm.

The replacement of bromine by iodine in position 3 displaces the maxima of the absorption spectra in chlorobenzene solution in the long-wave direction by 3–8 nm.

EXPERIMENTAL

3-Iodoacenaphthene. With cooling to 0°–2° C and stirring, a solution of 6.9 g (0.1 mole) of sodium nitrite in 60 ml of water was added dropwise over 12–15 min to a solution of 26.7 g (0.06 mole) of 3-aminoacenaphthene sulfate in 200 ml of 20% sulfuric acid. Stirring was continued for 25–30 min and then 200–250 ml of water cooled to 2°–3° C ml was added and the mixture was filtered. The diazonium solution was poured with stirring into a solution of 30 g (0.2 mole) of potassium iodide in 100 ml of water. The precipitated diazonium iodide was filtered off, well pressed out, and transferred to a beaker, 50–60 ml of acetone was added and when the vigorous evolution of nitrogen had ceased the mixture was heated in the water bath to the boil. After cooling, the crystals that had deposited were filtered off and dried. This gave 24.5 g (87.5%) of 3-iodoacenaphthene.

3-Iodoacenaphthenequinone (II). Sixty grams (0.2 mole) of sodium dichromate was added to a boiling solution of 28 g (0.1 mole) of 3-iodoacenaphthene in 200 ml of glacial acetic acid. The reaction took place at 115°–118° C for 10 min. Then the mixture was diluted with water and the precipitate of oxidation products was filtered off. To isolate the 2-iodonaphthalic acid, the precipitate was treated with 6% sodium carbonate solution (2 × 200 ml) with heating on the water bath for 35–40 min and the mixture was filtered. The residue was treated with a 40% solution of sodium bisulfite (2 × 20 ml) with heating in the water bath for 40 min. Concentrated hydrochloric acid was added to the resulting bisulfite solution and the mixture was boiled to eliminate sulfur dioxide. The precipitate that deposited was filtered off, washed with water, and dried. The yield of II was 7.2 g (23.3%). Golden-yellow needles with mp 226°–227° C (from acetic acid). Found, %: I 41.01. Calculated for $C_{12}H_5IO_2$, %: I 41.19.

2-Iodonaphthalic anhydride (III). Sixty grams (0.2 mole) of sodium dichromate was added to a solution of 28 g (0.1 mole) of 3-iodoacenaphthene in 600 ml of glacial acetic acid, and the mixture was

Some Properties of the Dyes Obtained

Compound	Mp, ° C	λmax, nm (in chlorobenzene)	Empirical formula	Element	Found, %	Calculated, %	Yield, %
IV	308—309	300, 480, 507	$C_{20}H_9BrO_2S$	Br	20.08	20.32	82.7
V	283	308, 485, 518	$C_{20}H_9BrO_2S$	Br	20.49	20.32	91.5
VI	351—352	302, 477, 510	$C_{20}H_8BrClO_2S$	Br	18.76	18.68	85.0
VII	352—353	309, 483, 511	$C_{20}H_8BrClO_2S$	Br	18.46	18.68	92.0
VIII	318—319	302, 477, 505	$C_{21}H_{10}BrClO_2S$	Br	18.32	18.54	89.2
IX	322—324	306, 477, 511	$C_{21}H_{10}BrClO_2S$	Br	18.43	18.54	95.9
X	275—276	305, 366, 458	$C_{22}H_{13}BrO_3S$	Br	18.01	18.27	89.3
XI	246—248	306, 365, 465	$C_{22}H_{13}BrO_3S$	Br	18.42	18.27	96.1
XII	>360	332, 386, 438	$C_{24}H_{11}BrO_2S$	Br	18.28	18.02	84.5
XIII	>360	333, 390, 442	$C_{24}H_{11}BrO_2S$	Br	18.30	18.02	87.8
XIV	304—305	303, 477, 512	$C_{20}H_9IO_2S$	I	28.71	28.83	89.0
XV	331—332	304, 476, 513	$C_{20}H_8ClIO_2S$	I	26.58	26.73	91.0
XVI	329—330	302, 477, 513	$C_{21}H_{10}ClIO_2S$	I	26.49	26.61	90.5
XVII	299—300	303, 363, 463	$C_{22}H_{13}IO_3S$	I	26.34	26.20	89.1
XVIII	>360	335, 388, 442	$C_{24}H_{11}IO_2S$	I	25.70	25.88	88.0
XIX	335—336	310, 405, 555	$C_{20}H_{10}BrNO_2S$	Br	19.42	19.55	76.2
XX	330—332	302, 402, 552	$C_{20}H_{10}BrNO_2S$	Br	19.69	19.55	71.8
XXI	250—252	300, 405, 555	$C_{20}H_{10}INO_2S$	I	29.84	29.98	78.6

heated in the water bath for 1 hour. Then it was diluted with water and filtered, and the residue was treated with 6% sodium carbonate solution (3 × 200 ml). The sodium carbonate solution was acidified with hydrochloric acid and the III that precipitated was filtered off and dried. Yield 24.7 g (76%), mp 256°-257° C (from nitrobenzene). Found, %: I 38.98. Calculated for $C_{12}H_5IO_3$, %: I 39.16.

2-Iodonaphthalimide. A mixture of 3.24 g (0.01 mole) of III, 30 ml of 20% aqueous ammonia, and 3 ml of nitrobenzene was heated at 35°-40° C for 15 min and was then boiled for 30 min. The nitrobenzene was distilled off with steam and the precipitate was filtered off, washed with water, and dried. This gave 2.8 g (86.6%) of the imide. Yellow needles, mp 313°-314° C (from nitrobenzene). Found, %: N 4.48. Calculated for $C_{12}H_6INO_2$, %: N 4.33.

3-Bromoacenaphthene was obtained with a yield of 55.6% in a similar manner to 3-iodoacenaphthene.

3-Bromoacenaphthenequinone (I). Eighty grams (0.27 mole) of sodium dichromate was added to a boiling solution of 23.3 g (0.1 mole) of bromoacenaphthene in 200 ml of glacial acetic acid. After the vigorous reaction had ceased, the mixture was diluted with water and the precipitate was filtered off and treated further as described in the synthesis of II. This yielded 8.4 g (32%) of I in the form of golden yellow needles with mp 239°-240° C (from acetic acid). Found, %: Br 30.22. Calculated for $C_{12}H_5BrO_2$, %: Br 30.60.

Condensation of 3-bromo-, 3-iodo-, and 5-bromoacenaphthenequinones with 3-hydroxythionaphthene and its derivatives. A solution of 0.01 mole of a substituted acenaphthenequinone and 0.01 mole of 3-hydroxythionaphthene or one of its derivatives in 50 ml of glacial acetic acid was boiled for 10 min in the presence of 0.2 ml of concentrated hydrochloric acid; a voluminous precipitate of a dye (IV-XII) deposited immediately. After cooling, the dye was filtered off and crystallized from nitrobenzene.

Condensation of 3-bromo-, 3-iodo-, and 5-bromoacenaphthenequinones with indoxyl. A filtered solution of 19 g of a 7% indoxyl melt in 100 ml of 70% acetic acid was added to a solution of 2.6 g of a substituted acenaphthenequinone in 150 ml of glacial acetic acid. The mixture was boiled for 5 min and, after cooling, the crystals of dye (XIX-XXI) that had deposited were filtered off, washed with water, and dried. They were recrystallized from nitrobenzene.

REFERENCES

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