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Studies on Some Thioindigoid Dyestuffs

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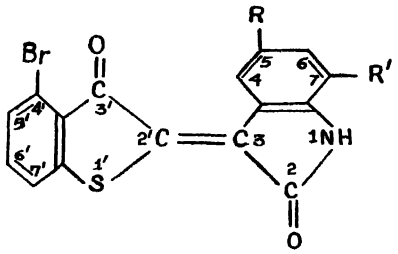
4-Bromo-3-hydroxy-thionaphthene was synthesised and condensed with isatin and its 5-chloro-, 5-bromo-, 5-iodo-, 5-nitro-, 5:7-dibromo-, 5-bromo-7-nitro- and 5:7-dinitro derivatives. These newly prepared 3-indole-2′ (4′-bromo) thionaphthene indigos were compared with the previously known corresponding 5′-bromo-, 6′-bromo- and 7′-bromo- dyes with respect to their colour and absorption maxima. The depth of colour was found to run as under 5′-bromo dye > 7′-bromo dye > 4′-bromo dye > 6′-bromo dye.

IN previous communications Guha and co-workers[1-3], have reported the synthesis and properties of 3-indole-2′ (5′-,6′-, and 7′-bromo) thionaphthene indigos. In this communication, we report the preparation and properties of eight 3-indole-2′ (4′-bromo) thionaphthene indigos in order to determine the influence of a bromine atom, on the depth of colour when present in all the available positions i.e., (4′- to 7′-) of the thionaphthene moiety of the parent dye, 3-indole-2′-thionaphthene indigo, generally known as Thioindogo Scarlet (I),



I R = R′ = H
II R = Br; R′ = H
III R = I; R′ = H
IV R = NO_2; R′ = H
V R = Cl; R′ = H
VI R = R′ = Br
VII R = Br; R′ = NO_2
VIII R = R′ = NO_2

by a study of the colour and absorption maxima of these newly prepared dyes and by comparison with the available data of the previously reported isomeric dyes.

For the purpose, the hitherto unknown, 4-bromo-3-hydroxythionaphthene was first prepared, by internal Friedel-Craft cyclisation of the acid chloride of *m*-bromophenyl thioglycollic acid and obtained in 27 to 30% yield as colourless needles, m.p. 147°.

Cyclisation of the acid chloride at the alternative position namely *para* to the bromine atom would give rise to the known 6-bromo-3-hydroxythionaphthene (m.p. 158°). The identity of the 4-bromo compound was established by (a) its m.p. (147°), which was depressed on admixture with the -6-bromo compound, and by (b) comparison of colour, m.p. and I.R. spectra of some condensation products obtained by condensing the 4-bromo and the 6-bromo compounds separately, using the same substrate in both the cases.

4-Bromo-3-hydroxythionaphthene was next condensed with isatin and its 5-chloro-, 5-bromo-, 5-iodo-, 5-nitro-, 5 : 7-dibromo-, 5-bromo-7-nitro-, and 5 : 7-dinitro-derivatives and the dyes were obtained in 70–90% yield. These brown, dark brown and violetish brown, crystalline dyes are all soluble in nitrobenzene and pyridine, moderately soluble in xylene and toluene and slightly soluble in chloroform, carbon tetrachloride and acetic acid. They dissolve in cold concentrated H_2SO_4 producing intense dark brown or dark violet-red colour. Reduction by sodium hydrosulphite at different temperatures, proved difficult and the shades could not be fully developed on cotton.

The absorption maxima values of some of these dyes compare well with the available data of some of the isomeric 5-, 6- and 7-bromo dyes[1,2,3]. It is now possible to arrange the depth of colour of these isomeric dyes in the following order : 5-bromo dye > 7-bromo dye > 4-bromo dye > 6-bromo dye. The position of the parent dye i.e., Thioindigo Scarlet is next to the 6-bromo dye, and so it can now also be concluded that introduction of a bromine atom in the thionaphthene moiety of the parent dye invariably produces deepening of colour.

Experimental

Preparation of 4-Bromo-3-hydroxy-thionaphthene :

3-Bromophenylthioglycollic acid (2 g) were dissolved in chlorobenzene (15 ml) by heating to 70°. Phosphorus trichloride (3 ml) was added to this warm solution and the mixture was kept stirred at 70° for 1 hr. It was next cooled to 20° and powdered

TABLE

T = Thionaphthene indigo; I = Isatin; A = 4-Bromo-3-hydroxy thionaphthene

Sl. No.	Name of Dye	Reactants	Appearance Yield %	Colour with conc. H_2SO_4	Formula	λ_{max} in mμ
1.	3-Indole-2′-(4′-bromo) T	A+I	Brown 78%	Deep violet brown	$C_{16}H_8BrNO_2S$	503
2.	3-(5-Bromo) indole-2′-(4′-bromo) T	A+5-bromo-I	Violetish brown 72%	Dark brown	$C_{16}H_7Br_2NO_2S$	504
3.	3-(5-Iodo) indole-2′-(4′-bromo) T	A+5-iodo-I	Darkish brown 75%	Blackish brown	$C_{16}H_7BrINO_2S$	505
4.	3-(5-Nitro) indole-2′-(4′-bromo) T	A+5-nitro-I	Brown 70%	,,	$C_{16}H_7BrN_2O_4S$	505
5.	3-(5-Chloro) indole-2′-(4′-bromo) T	A+5-chloro-I	Darkish brown 74%	,,	$C_{16}H_7BrClNO_2S$	498
6.	3-(5 : 7-Dibromo) indole-2′-(4′-bromo) T	A+5 : 7-dibromo-I	Violet brown 78%	Yellowish brown	$C_{16}H_6Br_3NO_2S$	507
7.	3-(5-Bromo-7-nitro) indole-2′-(4-bromo) T	A+5-bromo-7-nitro-I	Violet brown 82%	Blackish brown	$C_{16}H_6Br_2N_2O_4S$	510
8.	3-(5 : 7-Dinitro)-indole-2′-(4′-bromo) T	A+5 : 7-dinitro-I	Chocolate brown 80%	,,	$C_{16}H_6BrN_3O_6S$	518

anhydrous aluminium chloride (6 g) were cautiously added in four to five instalments with shaking. The mixture was then warmed again to 70° and maintained at that temperature for three hours with stirring. After the reaction, the mixture was decomposed with crushed ice (50 g) and subjected to steam distillation. The aqueous distillate, collected after the removal of chlorobenzene, gave on filtration 4-bromo-3-hydroxythionaphthene as colourless needles m.p. 147°, yield 0.5 to 0.55 g (Found : C, 42,3; H, 2.4. C_8H_5BrOS requires C, 41.9; H, 2.2%). Melting point was depressed on admixture with authentic 6-bromo-3-hydroxy thionaphthene.

Preparation of the dyes

The 4-bromo dyes were all prepared by refluxing for 15–20 mins. equimolecular quantities of the appropriate isatin and 4-bromo-3-hydroxy thionaphthene in glacial acetic acid solution in presence of 2–3 ml conc. HCl. The precipitated dyes were filtered, washed, dried and crystallised from pyridine. All the dyes melted above 300°. Absorption maxima values were determined in pyridine solution. Other details are given in the Table.

Elemental analysis of the dyes reported herein agree well with the required analytical values.

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