LXXIX.—*Dyes derived from Acenaphthenequinone. Part II. Azine and Azonium Derivatives.*

By Sisir Kumar Guha.

In continuation of the work of Sircar and Guha (J., 1924, **125**, 335) the following azine and azonium derivatives have been prepared by the condensation of 3-chloroacenaphthenequinone (Dziewonski and Zahrzewska-Baranowska, *Bull. Acad. Polonaise*, 1927, **3**, *A*, 65) and 3-bromoacenaphthenequinone (Graebe and Guinsbourg, *Annalen*, 1903, **327**, 87; Dziewonski, Schoenovna, and Glaznerovna, *Bull. Acad. Polonaise*, 1929, *A*, 636) with various *o*-diamines: 3-*chloro*- and 3-bromo-acenaphthaphenazine, 3-*chloro*- and 3-*bromo-acenaphthatolazine*, 3-*chloro*- and 3-*bromo-acenaphthanaphthazine*, 3-*chloro*- and 3-*bromo-acenaphthaphenazinazine*, 3-*chloro*- and 3-*bromo-acenaphthanaphthazine-5′-sulphonic acid*, and *phenyl-3-chloroacenaphthanaphthazonium nitrate*.

These compounds have been obtained in well-defined crystalline forms. Except the last three, they are all insoluble in water but dissolve in concentrated sulphuric acid, giving solutions with characteristic colours from which they are precipitated by water as light flocculent masses suitable for dyeing wool from an acid bath. The dyed shades range from lemon-yellow to light chocolate and are quite even. The colours in the case of azines obtained from 3-bromoacenaphthenequinone are decidedly deeper than those of the corresponding chloro-derivatives.

The tinctorial properties of some of these compounds are not less developed than those of the available, most nearly corresponding phenanthraquinone derivatives (Sircar and Dutt, J., 1922, **121**, 1944; *J. Indian Chem. Soc.*, 1924–25, **1**, 201; Dutt, J., 1922, **121**, 1952):

Compound.	Dyeing shade on wool.
3-Bromoacenaphthanaphthazine	Lemon-yellow
2 : 7-Dibromophenanthranaphthazine	Light yellow
3-Bromoacenaphthaphenazinazine	Light chocolate
2-Bromophenanthraphenazinazine	Reddish-brown
Phenyl-3-chloroacenaphthanaphthazonium nitrate	Yellowish-orange
3-Bromonaphthaflavinduline (nitrate)	Orange

EXPERIMENTAL.

3-*Bromoacenaphthenequinone.*—The yield obtained in the following process is three times as large as that obtained by Graebe and Guinsbourg's method (*loc. cit.*).

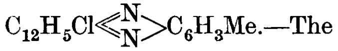
3-Bromoacenaphthene (Crompton and Walker, J., 1912, **101**, 958) (5 g.) in 45 c.c. of glacial acetic acid at 100—118° is rapidly oxidised with 10 g. of well-fused, very finely powdered sodium dichromate. The brick-red precipitate produced on addition of hot water is collected and well stirred for 90 minutes with 35 c.c. of 10% sodium carbonate solution at 75—85°, and is then repeatedly extracted with small quantities of boiling dilute sodium bisulphite solution. The combined extracts are stirred at 65° and the liquid is filtered. This treatment eliminates 4-bromonaphthalic anhydride, the last trace of which is not removed by the alkali. The crystalline bisulphite compound is washed with water and decomposed by boiling dilute sulphuric acid. The 3-bromoacenaphthenequinone crystallises from glacial acetic acid in yellow needles (1·1—1·2 g.), m. p. 238° (G. and G. record m. p. 194°; D., S., and G., *loc. cit.*, give m. p. 235—236°) (Found: Br, 30·7. Calc.: Br, 30·65%).

The monophenylhydrazone, obtained from the quinone and phenylhydrazine in boiling alcohol, crystallised from glacial acetic acid in vermilion needles, m. p. 180° (D., S., and G., give m. p. 179—180°) (Found: N, 8·2. Calc.: N, 8·0%).

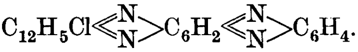
3-*Chloroacenaphthaphenazine*,  $C_{12}H_5Cl\Big\langle\begin{matrix}N\\N\end{matrix}\Big\rangle C_6H_4$, separated immediately in light cream-coloured, silky, rectangular plates when 3-chloroacenaphthenequinone (0·43 g.) and *o*-phenylenediamine (0·22 g.) were heated in 35 c.c. of boiling glacial acetic acid.

It was boiled with alcohol, in which it was only sparingly soluble, and recrystallised from glacial acetic acid ; m. p. 278°. It is a light, fibre-like substance, soluble in benzene and pyridine, sparingly soluble in acetone, and gives a reddish-brown solution in concentrated sulphuric acid (Found : N, 10·0. $C_{18}H_9N_2Cl$ requires N, 9·7%).

3-Bromoacenaphthaphenazine, similarly prepared and purified, crystallised in light cream-coloured, silky needles, m. p. 272° (D., S., and G., *loc. cit.*, record m. p. 261—263°) (Found : N, 8·55. Calc. : N, 8·4%).

3-*Chloroacenaphthatolazine*,  $C_{12}H_5Cl{<}\substack{N\\N}{>}C_6H_3Me$.—The dark brown solution produced by boiling 3-chloroacenaphthenequinone (0·433 g.) and 3 : 4-tolylenediamine (0·244 g.) in 40 c.c. of glacial acetic acid for 10 minutes deposited, on standing, pale yellow crystals. The *azine* was purified by precipitation with water from glacial acetic acid solution, and repeated boiling with alcohol ; it then crystallised from amyl alcohol in cream-coloured needles, m. p. 256°, soluble in benzene, pyridine, and acetic acid, sparingly soluble in alcohol, acetone, and methyl alcohol. The solution in concentrated sulphuric acid is brownish-red (Found : N, 9·6. $C_{19}H_{11}N_2Cl$ requires N, 9·25%).

3-*Bromoacenaphthatolazine*, similarly prepared from 3-bromoacenaphthenequinone (0·78 g.) and the diamine (0·366 g.) in 52 c.c. of boiling glacial acetic acid, crystallised in cream-coloured needles, m. p. 270° (Found : N, 8·3. $C_{19}H_{11}N_2Br$ requires N, 8·1%).

3-*Chloroacenaphthaphenazinazine*,  $C_{12}H_5Cl{<}\substack{N\\N}{>}C_6H_2{<}\substack{N\\N}{>}C_6H_4$. —A solution of 3-chloroacenaphthenequinone (0·65 g.) and 2 : 3-diaminophenazine (0·63 g.) in glacial acetic acid (40 c.c.) was boiled for 20 minutes and kept over-night. The crystalline deposit was heated successively with a dilute solution of sodium bisulphite and with dilute acetic acid and washed with hot water. The *azine* does not melt. It gives a greenish-black solution in concentrated sulphuric acid and dyes wool in light chocolate shades from an acid bath. It is soluble in glacial acetic acid, aniline, pyridine and amyl alcohol, and sparingly soluble in benzene and alcohol (Found : N, 14·1. $C_{24}H_{11}N_4Cl$ requires N, 14·3%).

3-*Bromoacenaphthaphenazinazine*, similarly prepared from 3-bromoacenaphthenequinone (0·78 g.) and 2 : 3-diaminophenazine (0·63 g.) in 55 c.c. of boiling glacial acetic acid, separated from pyridine, on cautious addition of hot water, in rectangular crystalline aggregates. It dyes wool in light chocolate shades and resembles the preceding compound in properties (Found : Br, 18·4. $C_{24}H_{11}N_4Br$ requires Br, 18·4%).

3-*Chloroacenaphthanaphthazine*, $C_{12}H_5Cl{<}^{N}_{N}{>}C_{10}H_6$, crystallised when 3-chloroacenaphthenequinone (0·65 g.) and 1 : 2-naphthylenediamine (0·47 g.) were heated together in 26 c.c. of boiling glacial acetic acid. After being boiled with alcohol, it crystallised from pyridine in silky lemon-yellow rectangles, m. p. 274°, and from amyl alcohol in fine needles. It is soluble in chloroform, benzene, acetic acid, aniline, and pyridine, sparingly soluble in alcohol and acetone, forms a purple solution in concentrated sulphuric acid, and dyes wool in lemon-yellow shades from an acid bath (Found : N, 8·3. $C_{22}H_{11}N_2Cl$ requires N, 8·3%).

3-*Bromoacenaphthanaphthazine*, similarly prepared from 3-bromoacenaphthenequinone (0·52 g.) and the diamine (0·32 g.) in 35 c.c. of boiling glacial acetic acid, separated from pyridine in fine lemon-yellow needles, m. p. 266°. It dyes wool in pleasant lemon-yellow shades (Found : Br, 20·7. $C_{22}H_{11}N_2Br$ requires Br, 20·9%).

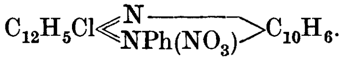
3-*Chloroacenaphthanaphthazine*-5′-*sulphonic Acid*,

$$C_{12}H_5Cl{<}^{N}_{N}{>}C_{10}H_5{\cdot}SO_3H.$$

—3-Chloroacenaphthenequinone (0·43 g.) and 1 : 2-naphthylenediamine-5-sulphonic acid hydrochloride (0·62 g.) were boiled together with 40 c.c. of dilute acetic acid (2*N* approx.) for 30 minutes : fine, silky, fibre-like, canary-yellow needles of the condensation product separated. Glacial acetic acid (8—10 c.c.) was added, the heating continued for 2 hours, and the liquid filtered hot. The crystals were washed with dilute acetic acid and a little water and dissolved in very dilute warm caustic soda solution, and the filtered solution was concentrated to a small volume and acidified with dilute hydrochloric acid; brownish-yellow flocks, not melting below 300°, were deposited. The *acid* is soluble in water, slightly soluble in glacial acetic acid and alcohol, and insoluble in benzene. Solutions in caustic alkalis or acetic acid solidify to a jelly on cooling. In concentrated sulphuric acid, the acid forms a blood-red solution. It dyes wool in light yellow shades (Found : N, 7·0. $C_{22}H_{11}O_3N_2ClS$ requires N, 6·7%).

3-*Bromoacenaphthanaphthazine*-5′-*sulphonic Acid*.—Finely powdered 3-bromoacenaphthenequinone (0·52 g.) was added to 70 c.c. of boiling dilute acetic acid (2*N* approx.), containing the diaminesulphonic acid hydrochloride (0·7 g.), and heated for 3 hours : silky, fibre-like, canary-yellow needles were produced. Glacial acetic acid (15 c.c.) was added, and the heating continued for 1 hour. The *substance* was purified through the sodium salt as in the preceding case (Found : Br, 17·4. $C_{22}H_{11}O_3N_2BrS$ requires Br, 17·3%).

Phenyl-3-chloroacenaphthanaphthazonium Nitrate,



$$C_{12}H_5Cl\left\langle\begin{matrix}N\text{———}\\NPh(NO_3)\end{matrix}\right\rangle C_{10}H_6.$$

—3-Chloroacenaphthenequinone (0·43 g.) and phenyl-1-amino-β-naphthylamine (0·47 g.), dissolved in hot glacial acetic acid, were treated with 2 c.c. of concentrated nitric acid and again heated for 2—3 minutes. The deep red solution, after treatment with ether, slowly deposited small yellow-orange needles of the condensation *product*. This was washed with ether and a little water and boiled with small quantities of dilute sodium bisulphite solution and alcohol. The *nitrate* melts and decomposes above 300°. It is somewhat soluble in boiling water, soluble in acetic acid, acetone, alcohol, and pyridine, and insoluble in benzene and ether. It gives a violet coloration with concentrated sulphuric acid and dyes wool in yellow-orange shades from an acid bath (Found : Cl, 7·2. $C_{28}H_{16}O_3N_3Cl$ requires Cl, 7·4%).

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