

## NAPHTHOQUINONE SERIES—PART I

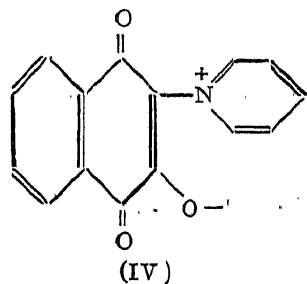
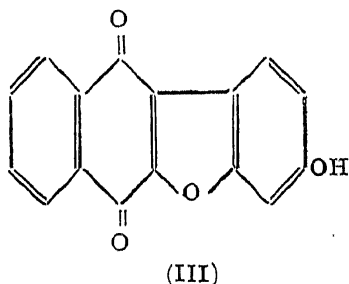
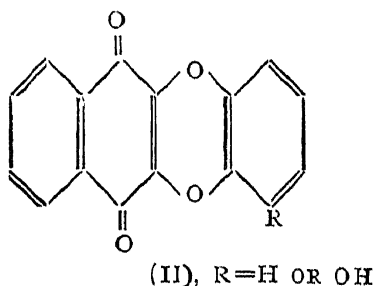
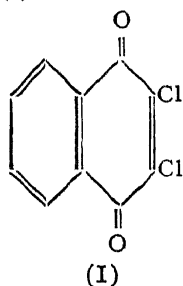
### Brazaquinone Vat Dyes from 2:3-Dichloro-1:4-Naphthoquinone : Part I Constitution of "iso-Dinaphthalene Oxide"

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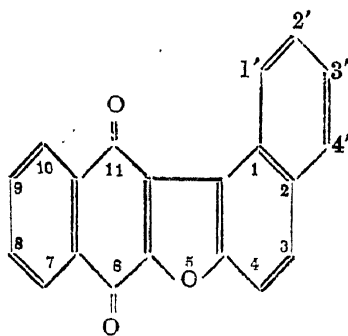
2:3-DICHLORO-1:4-NAPHTHOQUINONE (I) is marketed in U.S.A. under the name "Phygon" for use as an agricultural fungicide<sup>1</sup> and as an anti-mildew agent<sup>1</sup> for textiles. Of the several methods suggested for the preparation of (I), a convenient laboratory method<sup>2</sup> consists in sulphonation of  $\alpha$ -naphthol followed by treatment of the diluted sulphonation mixture with potassium chlorate and hydrochloric acid. The chlorine atoms in (I) being reactive and easily replaceable, a series of 3-chloro-2-substituted, 2:3-disubstituted and polycyclic derivatives of 1:4-naphthoquinone have been synthesized starting from (I).



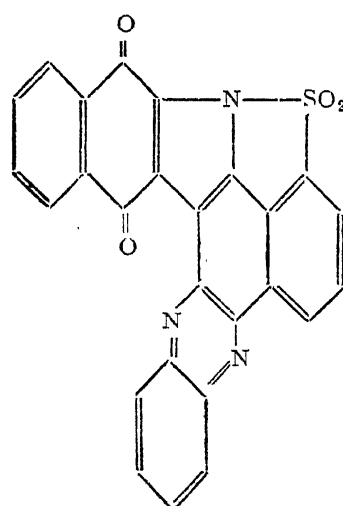
Both the chlorine atoms are replaced by condensation with phenol<sup>2</sup> in presence of sodium ethoxide to give 2:3-diphenoxy-1:4-naphthoquinone. It has now been observed that the diphenoxy derivative is also formed by condensation of (I) with phenol in pyridine. The chlorine atoms, likewise, react with the adjacent hydroxyl groups in catechol<sup>2</sup> and pyrogallol<sup>3</sup> leading to dioxine derivatives such as (II), although the structure assigned for the condensation product with pyrogallol needs further confirmation. With

resorcinol,<sup>4</sup> however, one of the chlorine atoms in (I) reacts with one hydroxyl group and the other removes the hydrogen atom from the reactive 4-position which is *o*-, *p*- to the hydroxyl groups in resorcinol, leading to the furan derivative, 3-hydroxy-6:11-brazanquinone\* (III). The above condensation was carried out by Graebe and Liebermann<sup>5</sup> in sodium ethoxide, but Eistert<sup>6</sup> has reported that the reaction may also be carried out in pyridine. It has, however, been noted by us that reaction in pyridine gives a very impure product from which only a small amount of (III) can be isolated, the major product formed being the betaine (IV). The formation of the betaine by the reaction of (I) with pyridine was first described by Ullmann and Ettisch<sup>2</sup> and the compound was later constituted as (IV) by Eistert.<sup>6</sup>

Eistert<sup>6</sup> has studied the use of (I) as an intermediate for the synthesis of vat dyes. Condensation of (I) with phenols containing a *meta*-substituent such as a hydroxy, amino, alkyl or aryl amino group gives 3-substituted brazanquinones. Reaction with  $\beta$ -naphthol gives 1:2-benzobrazanquinone (V). 1-Phenyl-3-methyl-5-pyrazolone and "4-hydroxy-1-methyl-2-picolone" react with (I) presumably in their enolic forms leading to complex dark-coloured furan derivatives. Thioindoxyl likewise gives a furanothio-naphthenonaphthoquinone derivative. The colour of these heterocyclic derivatives of furanonaphthoquinones was explained by Eistert on the basis of resonance between different betaine or meso-ionic structures. The above naphthoquinone derivatives prepared by Eistert vatted in alkaline hydro-sulphite solution but had poor substantivity to cotton.



(V)



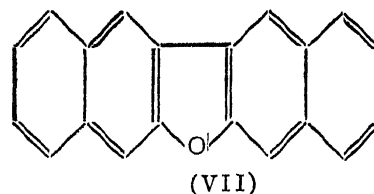
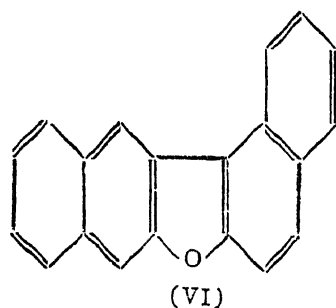
Indanthrene Yellow 6 GD

\* 2:3-Benzo-4:5-(2':3'-naphtho) furan is referred to as "brazan" in the literature from its derivation from brazilin.<sup>4</sup> 2:3(2':3'-Coumarano)-1:4-naphthoquinone is described as "brazanquinone". The trivial name "brazanquinone" has been used in this paper in common with other workers.

Indanthrene Yellow 6 GD,<sup>7</sup> a greenish yellow dye, is of interest as it is free from photochemical tendering activity and appears to be the only example of a commercial naphthoquinone vat dye. It is prepared by the condensation of (I) with the azine obtained by the reaction of the nitroso derivative of naphthasultam with *o*-phenylenediamine.

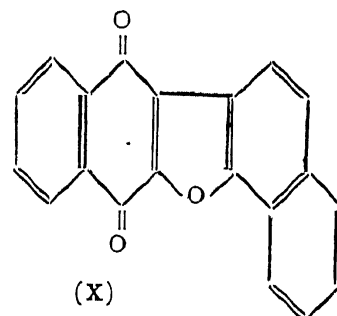
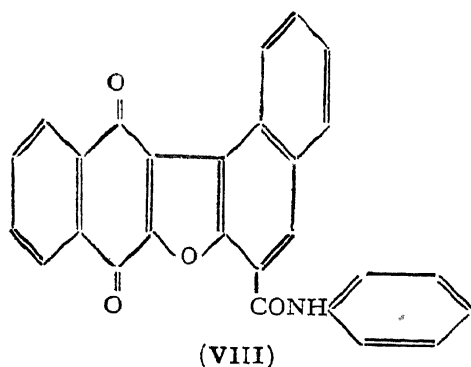
Substantive vat dyes have now been prepared by the reaction of (I) with bromo derivatives of  $\alpha$ - and  $\beta$ -naphthols and by condensation of (I) with 2-hydroxy-3-naphthanilide (Naphthol AS). It has been mentioned earlier that condensation of (I) with phenol in sodium ethoxide or pyridine gives 2:3-diphenoxy-1:4-naphthoquinone. Similar condensation of  $\beta$ -naphthol would therefore lead to either 1:2-di( $\beta$ -naphthoxy)-1:4-naphthoquinone or to 1:2-benzobrazanquinone (V). In view of the fact that resorcinol gives the furan derivative, 3-hydroxybrazanquinone and also in view of the reactivity of the  $\alpha$ -position in  $\beta$ -naphthol, it appears that the condensation product of (I) with  $\beta$ -naphthol is more likely to be constituted as (V) rather than the dinaphthoxy derivative. However, since the two compounds have nearly the same elementary composition, it is necessary to provide unambiguous proof as regards the furan structure (V) of the condensation product (A) obtained by the reaction of (I) and  $\beta$ -naphthol in pyridine. It is also a curious fact that the furan and the dinaphthoxy structures derived from (I) and Naphthol AS have also very nearly the same elementary composition.

“*iso*Dinaphthalene Oxide” (B), a dinaphthofuran obtained by prolonged heating of  $\beta$ -naphthol with alkali-earth oxides above 280°, was constituted by Clemo and Spence<sup>8</sup> as dinaphtho (2':3':2:3-) (1":2":4:5) furan (VI) in preference to the alternative linear structure (VII) on the basis of spectroscopic data<sup>9</sup> and its oxidation to a *p*-monoquinone. Since the condensation product (A) of (I) and  $\beta$ -naphthol in pyridine was identical with the quinone prepared from (B) by oxidation, Eistert<sup>6</sup> concluded that (A) is 1:2-benzobrazanquinone (V). However as the constitution of (B) itself is not unambiguously proved, the constitution of (A) suggested by Eistert<sup>6</sup> cannot, therefore, be regarded as settled. Buu-Hoï<sup>10</sup> has recently claimed to have provided proof in confirmation of Clemo and Spence's assumption by the synthesis of (B) by the zinc dust distillation of (A) and by demonstrating that “1-substituted-2-naphthols (for example, 1-methyl-2-naphthol)” do not give furan derivatives by reaction with (I). The latter observation shows that  $\beta$ -naphthol links with (I) in the 1- and not the 3-position. Buu-Hoï has, however, not described the product actually obtained in the reaction between (I) and a 1-substituted 2-naphthol.



More positive evidence as regards the constitution of (A) has now been obtained by studying the reaction of (I) with 1-bromo-2-naphthol in pyridine. The latter reaction gave a halogen-containing brownish-orange quinonoid reaction product together with a halogen-free substance which proved to be identical with (A). The 1-position in  $\beta$ -naphthol is thus involved in the reaction of  $\beta$ -naphthol with (I) and (A) is therefore constituted as the furan derivative, 1:2-benzobrazanquinone (V). The constitution of "isodinaphthalene oxide" as dinaphtho (2':3':2:3) (1":2":4:5) furan (VI) follows from its conversion to (V) by oxidation<sup>6</sup> and conversely by its synthesis from (V) by zinc dust distillation.<sup>10</sup>

Condensation of (I) (1 mole) with 1-bromo-2-hydroxy-3-naphthanilide<sup>11</sup> (1 mole) in pyridine gave a halogen-containing quinonoid compound. Using two moles of the bromo derivative a halogen-free substance was obtained which proved to be identical with the condensation product of Naphthol AS and (I) in pyridine. The 1-position in Naphthol AS is therefore involved in the reaction with (I) and the resulting condensation product is unambiguously constituted as the furan structure, 1:2-benzobrazanquinone-4-carboxyanilide (VIII) and not as a 2:3-dinaphthoxynaphtho-



quinone. The constitution of the halogen-containing quinones obtained by the condensation of (I) with 1-bromo-2-naphthol and 1-bromo-2-hydroxy-3-naphthanilide is under investigation. The condensation products obtained

from (I) and compounds of the Naphtol AS series<sup>12</sup> have likewise been constituted as brazanquinone derivatives such as (VIII) where both the hydroxy group and the coupling position in the naphthol are involved.

To study the effect of the introduction of a bromine atom in (V), 6-bromo-2-naphthol was condensed with (I) to give 3'-bromo-1:2-benzobrazanquinone (IX). The latter proved to be much more substantive than (V). Buu Hoi<sup>10</sup> has recently claimed to have prepared (IX), but the product obtained by him is impure as it melts much lower than the product described in the present paper. It is probable that the dye obtained by Buu Hoi is contaminated with the betaine (IV) which is also formed together with (IX).

3:4-Benzobrazanquinone<sup>13</sup> (X), prepared by condensation of (I) with  $\alpha$ -naphthol, is also weakly substantive to cotton although it is slightly more substantive as compared to (V). Reaction of 4-bromo-1-naphthol with (I) gave 2-bromo-3:4-benzobrazanquinone (XI) which had good substantivity and gave a bright yellow shade on cotton. The increase in substantivity by the introduction of a bromine atom in (X) was greater as compared to the increase in substantivity observed when bromine was introduced in (V). 4-Bromo-1-naphthol was obtained in a purer form (m.p. 128°) and in better yields (55%) by a modification of the method due to Fieser and Desreux<sup>14</sup> who have reported 23% yield of the bromo derivative, m.p. 120°.

The condensation of (I) with Naphtol AS was first carried out in presence of sodium ethoxide and alcohol. The resulting bright yellow dye (VIII) (m.p. 315–19°) has good fastness properties and possessed better substantivity to cotton than several brazanquinone vat dyes obtained from more substantive Naphthols.<sup>12</sup> Since a small amount of 2-chloro-3-hydroxy-1:4-naphthoquinone was formed in this reaction and as the yield of (VIII) was only 62%, suitability of other media for this reaction was studied. Reaction in toluene in presence of potassium carbonate as an acid-binding agent was unsuccessful. Condensation in diethylaniline gave poor yields (28.5%) of (VIII), (m.p. 312–15°). However when pyridine was used as the solvent, (VIII) was obtained in pure crystalline form but the yields were again not satisfactory (m.p. 315°; yield 41.9%) on account of the conversion of (I) to the betaine (IV). This drawback was overcome by carrying out the reaction in dry toluene using enough pyridine to react with the hydrochloric acid liberated in the reaction. This method led to higher yields (72–75%), but the product gave lower m.p. 294–97°, whereas the product obtained when pyridine was used as the solvent melted at 315°. In the above condensation pyridine may be substituted by diethylaniline but the yield of (VIII) was lowered. In the light of these experiments, pyridine was used in subsequent condensations of (I) with compounds of the Naphtol AS series.<sup>12</sup>

## EXPERIMENTAL

*Condensation of 2:3-dichloro-1:4-naphthoquinone (I) with 1-bromo-2-naphthol*

2:3-Dichloro-1:4-naphthoquinone (I) (2.27 g.) was added to a boiling solution of 1-bromo-2-naphthol (4.5 g.) in pyridine (20 c.c.). The dark brown reaction mixture was heated under reflux for 2½ hours and then cooled. On leaving it overnight at 0°, lustrous brown crystalline compound (1.1 g.), m.p. 243–46°, separated. The product was repeatedly extracted with boiling water to remove the betaine (III). The residue, m.p. 265–66°, crystallized from glacial acetic acid in brownish yellow needles (0.2 g.), m.p. 269°. The product was free from halogens and nitrogen and was found to be identical with 1:2-benzobrazanquinone (V). The aqueous extracts on concentration gave the betaine (0.5 g.).

The pyridine mother-liquor on dilution with alcohol (50 c.c.), gave a halogen-containing orange-brown residue (1.0 g.), m.p. 237–43°, which was collected, washed with alcohol and purified by extraction with boiling water as before. The betaine-free product (0.65 g., m.p. 237–39°) after 4 crystallizations from xylene gave brownish orange rectangular plates, m.p. 255.5–56° (Found: C, 67.0; H, 3.3; Cl, 13.5%). When tested according to Vogel<sup>15</sup> the compound was found to contain chlorine, but not bromine.

The pyridine-alcohol filtrate, after removal of the above product, was concentrated to a small bulk and poured into ice and hydrochloric acid when a tarry product separated. The mixture was filtered through cotton-wool and the tarry residue was repeatedly extracted with boiling water. The aqueous extracts on concentration and cooling gave the betaine (0.5 g.). The water-insoluble residue was dissolved in 10% sodium hydroxide, treated with Norit and filtered. The alkaline solution was saturated with carbon dioxide and allowed to stand. Fine colourless needles (2.0 g.), m.p. 70–75°, separated which were found to be identical with 1-bromo-2-naphthol.

*Condensation of 2:3-dichloro-1:4-naphthoquinone (I) with 1-bromo-2-hydroxy-3-naphthanilide*

*Method A.*—Compound (I) (1.1 g., 1 mol.) was added to a boiling solution of 1-bromo-2-hydroxy-3-naphthanilide (1.7 g., 1 mol.) in pyridine (25 c.c.). The yellow colour of the naphthol solution in pyridine after addition of (I) quickly changed to light green → bright green → dark green and finally to brown. The mixture was heated under reflux for 3 hours and left overnight at 0°. The yellow crystalline product (0.3 g.) which separated was washed with alcohol and recrystallized from pyridine when it gave yellow needles, m.p. 284–85°. The mother-liquor on further standing

gave a second crop of the yellow product (0.8 g.), m.p. 265–70°. After removal of the betaine (II) by extraction with boiling water, the latter gave a residue (0.7 g.), m.p. 283–84°, which was identical with the first crop. After three recrystallizations from xylene it gave yellow clusters of needles, m.p. 283–85° (Found: C, 66.6; H, 3.0; Cl, 9.7; N, 2.85%). The compound when tested according to Vogel<sup>15</sup> showed the presence of chlorine but not bromine.

The pyridine mother-liquor, after separation of the above product, was added to ice and hydrochloric acid. The tarry product which separated gave 0.2 g. of the betaine (IV) on extraction with boiling water. The water-insoluble residue was dissolved in alkali and the alkaline solution was clarified with Norit. Saturation of the clarified alkaline solution with carbon dioxide, gave 1-bromo-2-hydroxy-3-naphthanilide (0.2 g.).

*Method B.*—The above reaction was repeated using (I) (2.27 g., 1 mol.), 1-bromo-2-hydroxy-3-naphthanilide (6.9 g., 2 mols.) and pyridine (60 c.c.). The brown reaction mixture was refluxed for 3 hours and then cooled. The yellow product (0.8 g., m.p. 283–87°) which separated was collected and crystallized from xylene (200 c.c.) when it gave yellow needles, m.p. 290–97°, containing traces of halogens. Recrystallization from nitrobenzene gave a product melting at 295–99°. Repeated crystallization of this product from pyridine gave a halogen-free product, m.p. 315–16° which was identical with 1:2-benzobrazanquinone-4-carboxyanilide (VIII).

### 3:4-Benzobrazanquinone (X)

$\alpha$ -Naphthol (0.7 g.) and (I) (1.1 g.) were refluxed with pyridine (15 c.c.) for 3 hours. The dark brown reaction mixture was cooled in ice and the crystals which separated were collected, washed with alcohol and dried (0.9 g., yield 60%), m.p. 229–30°. Recrystallization from benzene-alcohol (1:1) gave yellow flat needles, m.p. 234° (Fieser and Brown<sup>13</sup> give m.p. 229–30°) (Found: C, 80.2; H, 3.6. Calc. for  $C_{20}H_{10}O_3$ : C, 80.5; H, 3.4%). The mother-liquor was added to concentrated hydrochloric acid (20 c.c.) and crushed ice (25 g.). The orange-yellow product (0.35 g.), m.p. 280–85°, which separated was found to be the betaine (IV).

### 4-Bromo-1-naphthol

Iodine (26 g.) was dissolved in a solution of bromine (5 c.c.) in glacial acetic acid (60 c.c.) by warming to 50°, under continuous agitation. The solution of iodine bromide was added dropwise to a solution of  $\alpha$ -naphthol (14 g.) in acetic acid (45 c.c.) in 15 minutes. The mixture was cooled externally with ice and connected to a water pump during the addition. After one

hour during which the flask was shaken occasionally, the mixture was poured gradually into a vigorously stirred solution of sodium bisulphite (18 g.) in water (700 c.c.) when most of the bromo derivative precipitated. The mixture was neutralized with sodium bicarbonate (160 g.) which was added cautiously during 1½ hours under continued agitation. The precipitate was collected, washed with water and dried (17.5 g.). Crystallization from 33% aqueous alcohol (800 c.c.) gave pale pink long needles, m.p. 128° (12 g., yield 55%). Fieser and Desreux<sup>14</sup> have reported 23% yield of the crystalline compound melting at 120°.

#### 2-Bromo-3:4-benzobrazanquinone (XI)

A mixture of 4-bromo-1-naphthol (2.2 g.), (I) (2.2 g.) and pyridine (20 c.c.) was refluxed for 3 hours. The golden yellow crystals which separated on cooling were collected, washed with alcohol and extracted with boiling water to remove the betaine. The product (1.5 g.), m.p. 269°, after three recrystallizations from benzene, gave yellow needles, m.p. 270–71° (Found: C, 63.8; H, 2.7.  $C_{20}H_9BrO_3$  requires C, 63.7; H, 2.4%). Concentration of the mother-liquor gave a further crop of the product (0.1 g.). Evaporation of the alcohol washings and the aqueous extracts gave the betaine (IV) (1.0 g.).

#### 3'-Bromo-1:2-benzobrazanquinone (IX)

6-Bromo-2-naphthol<sup>16</sup> (2.24 g.), (I) (2.27 g.) and pyridine (20 c.c.) were heated under reflux for 3 hours. The brown residue which separated on cooling in ice was collected, washed with alcohol and dried (2.25 g.), m.p. 275–80°. After repeated extraction with boiling water, lustrous brown plates (0.85 g.), m.p. 317–18°, were obtained as residue. Recrystallization from xylene gave lustrous orange yellow plates, m.p. 324° (Buu Hoï<sup>10</sup> quotes m.p. 308°) (Found: C, 63.9; H, 2.6.  $C_{20}H_9BrO_3$  requires C, 63.7; H, 2.4%).

#### 1:2-Benzobrazanquinone-4-carboxyanilide (VIII)

*Condensation in Presence of Sodium Ethoxide.*—Sodium (0.23 g.; was dissolved in absolute alcohol (50 c.c.) and Naphtol AS (2.6 g.) was added. The solution was heated to boil and a suspension of (I) (1.1 g.) in absolute alcohol (150 c.c.) was then added. The mixture was initially greenish yellow but soon turned dark yellow and yellow crystals started separating out. After refluxing for 3 hours, the mixture was cooled and filtered. The bright yellow crystalline residue was washed with hot water to remove sodium chloride and dried (1.3 g., yield 62%), m.p. 315–19°. It crystallized from pyridine in felted needles, m.p. 316° (Found: C, 77.8; H, 3.3; N, 3.9.  $C_{27}H_{15}NO_4$  requires C, 77.7; H, 3.6; N, 3.4%).



The alcoholic mother-liquor, on concentrating to 20 c.c. and neutralizing with conc. hydrochloric acid, gave unreacted Naphtol AS (1.7 g.), m.p. 238°. The filtrate on dilution with water gave 2-chloro-3-hydroxy-1:4-naphthoquinone (0.2 g.).

*Condensation in Diethylaniline.*—Naphtol AS (1.3 g.), (I) (1.1 g.) and diethylaniline (15 c.c.) were refluxed for 2 hours and then cooled. The yellow needles which separated were collected, washed with alcohol and dried (0.6 g.), m.p. 312–15° (yield 28.5%). Mixed m.p. with the product obtained in the above experiment was not depressed.

*Condensation in Pyridine.*—Naphtol AS (5.3 g.), (I) (4.5 g.) and pyridine (50 c.c.) were refluxed for 3 hours and cooled. The yellow felted needles obtained were washed with alcohol and dried (3.5 g.), m.p. 315°; raised to 316° by recrystallization from pyridine. The product was purer than the products obtained by the above methods.

*Condensation in Toluene and Pyridine.*—Finely powdered sample of (I) (2.25 g.) and Naphtol AS (2.63 g.) and dry toluene (150 c.c.) were heated to boil under reflux and pyridine (4 c.c.) was added dropwise in 3 hours. After refluxing for 24 hours, toluene was removed by steam distillation and the yellow residue was collected, extracted successively with boiling water, cold and then boiling 10% aqueous sodium hydroxide and finally washed with water and dried (3.05 g., yield 72.5%), m.p. 294–97°. On crystallization from pyridine, the product gave yellow felted needles, m.p. 316°.

The aqueous extracts on evaporation gave the betaine (IV) (0.15 g.). The cold alkaline extract when neutralized with acid gave the unreacted naphthol (0.25 g.) and the hot alkaline extracts gave a mixture of the naphthol and 2-chloro-3-hydroxy-1:4-naphthoquinone (0.8 g.).

In the above experiment if diethylaniline (3 c.c.) was used in place of pyridine, the yield of (VIII) was only 45%.

#### *Colour Reactions and Dyeing Properties*

The colour in sulphuric acid, the colour of the vats, the shades on cotton and the fastness properties of the dyes are given in Table I.

Dyes (V), (IX), (X) and (XI) give greenish blue solutions in sulphuric acid. All of them are reduced easily by alkaline hydrosulphite and are applied to cotton by the IW or the IN process. The dyes gave yellow shades of poor to moderate fastness properties.

The dye (VIII) is difficult to reduce but after precipitation from sulphuric acid it vats readily at 60–70°. It gives a bright orange yellow shade with good fastness properties.

TABLE I

Compound	Colour in sulphuric acid	Colour of the vat	Shade on cotton	Fastness		
				Light	Severe Washing	Chlorine
V	Greenish blue	Orange	Pale brownish yellow	2-3	..	..
IX	Bluish green	Red-brown	Yellow	4-5	2-3	4
X	Blue	Brownish yellow	Pale yellow	2-3	1	3
XI	Greenish blue	Orange red	Bright yellow	2-3	3	4-5
VIII	Blue	Deep red brown	Bright orange yellow	5-6	5	5

Fastness to light was found using the Atlas Fade-O-Meter and following the standards of Society of Dyers and Colourists<sup>17</sup> and fastness to washing and chlorine by the I.C.I. method.<sup>18</sup>

## SUMMARY

Brazanquinone vat dyes have been prepared by the condensation of 2:3-dichloro-1:4-naphthoquinone (I) with  $\alpha$ - and  $\beta$ -naphthols and their bromo derivatives and by the condensation with Naphtol AS. Reaction of 1-bromo-2-naphthol with (I) in pyridine gave a halogenonaphthoquinone together with a halogen-free naphthoquinone which proved to be identical with the reaction product (A) obtained from (I) and  $\beta$ -naphthol in pyridine. The 1-position in  $\beta$ -naphthol is thus involved in the condensation with (I) and (A) is therefore constituted as the furan derivative, 1:2-benzobrazanquinone (V). Constitution of "iso-dinaphthalene oxide" as dinaphtho-(2':3':2:3-) (1":2":4:5) furan (VI) follows from its conversion to (V) by oxidation and conversely by its synthesis from (V) by zinc dust distillation. The condensation product of (I) with Naphtol AS is likewise the furan derivative 1:2-brazanquinone-4-carboxyanilide (VIII) since it is also formed from 1-bromo-2-hydroxy-3-naphthanilide by loss of bromine.

Introduction of bromine in (V) and 3:4-benzobrazanquinone and the introduction of the carboxyanilide group in (V) leads to more substantive dyes. The dyes give yellow and orange yellow shades. Fastness properties of the dyes have been determined.

We are indebted to Professor Louis F. Fieser of the Harvard University, for the generous gift of 2:3-dichloro-1:4-naphthoquinone used in the present and in the subsequent work. Our thanks are also due to the Council of Scientific and Industrial Research for the award of a Fellowship to one

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