

RANEY NICKEL REDUCTIONS

Part IV. Thioindigo Dyes, Thionaphthenes and Thiafluorenes

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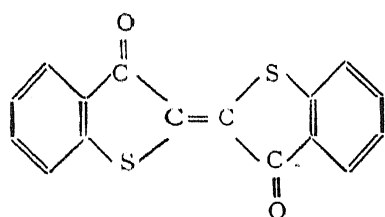
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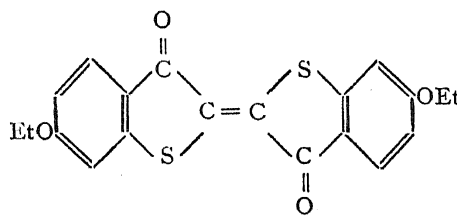
DESULPHURIZATION of thioindigo (Durindone Red B), 6:6'-diethoxythioindigo (Durindone Orange R) and thioindoxyl by the action of Raney alloy in aqueous alkali was discussed in Part II.¹ This method is useful for the determination of the constitution of sulphur-containing dyes and other organic compounds, and for the preparation of some of the products, such as the diphenacyl and 1:4-diphenylbutane derivatives, which are difficult to prepare by known methods. The latter may be expected to be formed by the desulphurization of the thioindigoid dyes, followed by reduction of the resulting sulphur-free compounds.

Degradation of thioindigoid dyes by treatment with alcoholic caustic potash,² ozonization,³ and oxidation with fuming nitric acid,⁴ involves the fission of the carbon chain linking the two aryl residues. Desulphurization of thioindigoid dyes by means of Raney nickel has the distinctive feature that the carbon skeleton of the molecule remains largely intact. Thus desulphurization of thioindigo (I) and 6:6'-diethoxythioindigo (II) by Raney alloy in aqueous alkali gave diphenacyl and 4:4'-diethoxydiphenacyl as the major products, although small amounts of benzoic acid, *p*-ethoxybenzoic acid and other by-products, were also obtained. Thioindigo gave 1:4-diphenylbutane when excess of Raney alloy was used. The present paper deals with the desulphurization of (I) and (II) under modified conditions, of other thioindigoid dyes, and of heterocyclic compounds containing sulphur as a part of the ring system.

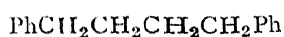
Desulphurization of thioindigoid dyes with Raney alloy in aqueous alkali gave several reduction products, but treatment with Raney nickel in alcohol gave 1:4-diphenylbutanes, which were formed in good yields and were the only products isolated. Thus thioindigo gave 1:4-diphenylbutane (III) (yield 76%) and 6:6'-diethoxythioindigo gave 1:4-bis-*p*-ethoxyphenylbutane (IV) (yield 59%). The constitution of (III) and (IV) was proved by oxidation to benzoic acid and *p*-ethoxybenzoic acid.



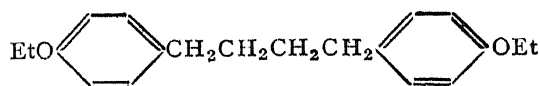
(I)



(II)

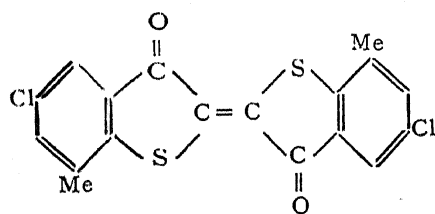


(III)

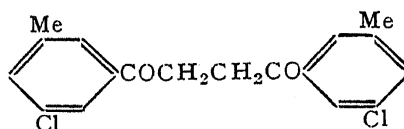


(IV)

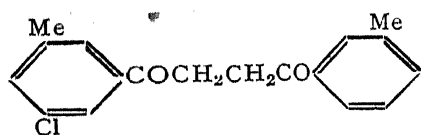
Treatment of 5:5'-dichloro-7:7'-dimethylthioindigo (Durindone Red 3BS) by Raney alloy in aqueous alkali left the dye largely unaffected, and it was found necessary to vat the dye before treatment with Raney alloy. When the dye, obtained in finely divided form by precipitation from sulphuric acid, was vatted with glucose and aqueous caustic soda and then treated with Raney alloy, the isolable sulphur-free degradation products were 3:3'-dichloro-5:5'-dimethyldiphenacyl (V), 5-chloro-3:3'-dimethyldiphenacyl (VI) and 1:4-di-*m*-tolyl-1-butanol (VII). When the dye was vatted by sodium hydrosulphite and aqueous alkali and then desulphurized by Raney alloy, a larger yield of the desulphurized product was obtained from which (V) and (VI) were again isolated, but the major constituent was a chlorine-free liquid which was not identified. Desulphurization of the dye by Raney nickel in boiling alcohol gave 1:4-di-*m*-tolylbutane (VIII), the constitution of which was confirmed by oxidation to isophthalic acid. Cyclization of the diphenacyl derivative (V) gave 2:5-di-(3'-chloro-5'-methyl)phenylfuran (IX).



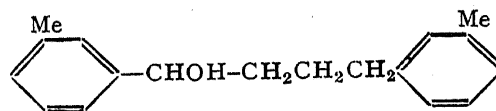
Durindone Red 3BS



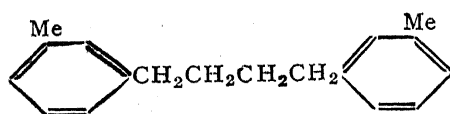
(V)



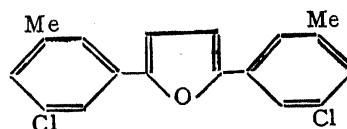
(VI)



(VII)

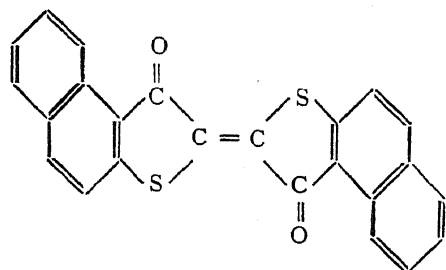


(VIII)

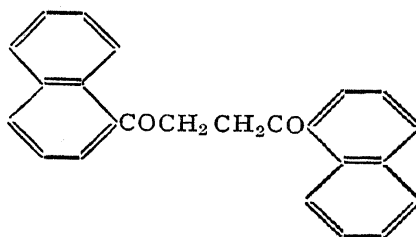


(IX)

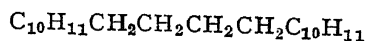
Reduction of Durindone Brown GS (X), the naphthalene analogue of thioindigo, with Raney alloy in aqueous alkali gave 1:2-di- α -naphthoylethane (XI) and a yellow non-fluorescent liquid (b.p. 140–2°/12 mm.) which analysed for 1:4-di- α -tetralylbutane (XII). Cyclization of (XI) gave 2:5-di- α -naphthylfuran (XIII). When the dye was desulphurized with Raney nickel in alcohol a colourless liquid (b.p. 215–20°/1 mm.), exhibiting a blue fluorescence, was obtained, and it analysed for 1:4-di- α -tetralylbutane (XII). The two di- α -tetralylbutanes are apparently the 1:2:3:4- and 5:6:7:8-tetrahydronaphthalene derivatives.



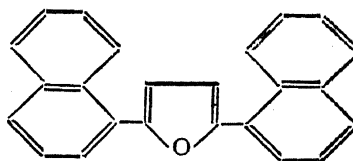
(X)



(XI)

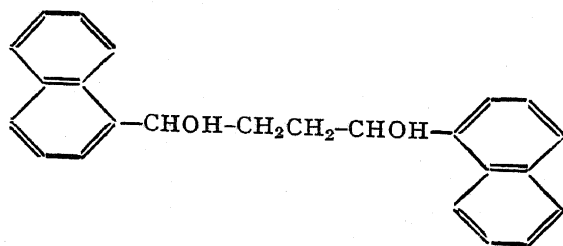


(XII)



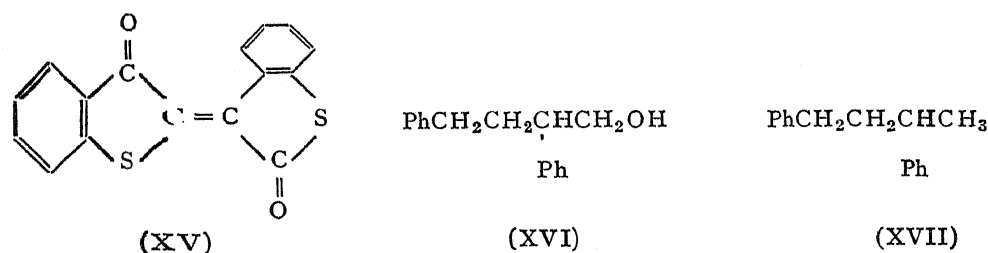
(XIII)

Ciba Brown 2R has been mentioned by Fox⁵ as equivalent to Indanthrene Printing Brown 3R which is 2-(4:5-benzothionaphthene)-3'-(6'-chloro-7'-methylindole)-indigo; but elementary analysis of purified Ciba Brown 2R and the shade on cotton indicate that it is probably identical with Durindone Brown GS (X). This was confirmed by desulphurization with Raney alloy in aqueous alkali and with Raney nickel in alcohol, when Ciba Brown 2R gave the same reduction products as Durindone Brown GS. In one experiment Raney alloy alkali reduction of Ciba Brown GS also gave a small amount of a substance which was probably the diol (XIV).

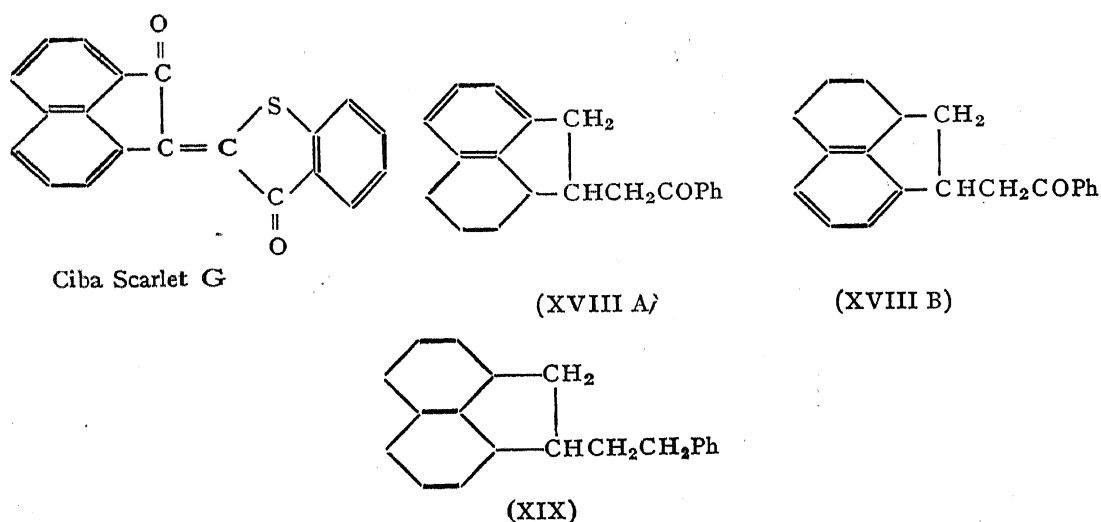


(XIV)

The desulphurization of unsymmetrical dyes was next studied. On treatment with Raney alloy in aqueous alkali 2:3'-bis-thionaphthene-indigo (XV) gave a compound which is probably constituted as 2:4-diphenyl-1-butanol (XVI). The alternative structure 1:3-diphenyl-1-butanol is improbable because Papa *et al.*⁶ have shown that, under the conditions employed, a carbonyl group attached to a benzene nucleus is reduced to CH_2 , whereas a carbonyl group not directly attached to the aryl residue undergoes reduction to an alcoholic group. Desulphurization of (XV) with Raney nickel in alcohol gave 1:3-diphenylbutane (XVII).

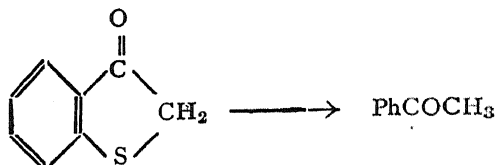


Desulphurization of Ciba Scarlet G by treatment with Raney alloy in aqueous alkali gave a complex mixture from which was isolated a pale yellow liquid, which analysed for $\text{C}_{20}\text{H}_{20}\text{O}$ and which probably has the structure (XVIII A) or (XVIII B). Desulphurization of the dye by Raney nickel in alcohol gave a hydrocarbon, $\text{C}_{20}\text{H}_{28}$, which may be represented as α -perhydro-acenaphthenyl- β -phenylethane (XIX). Attempts to dehydrogenate (XIX) by treatment with selenium were unsuccessful.

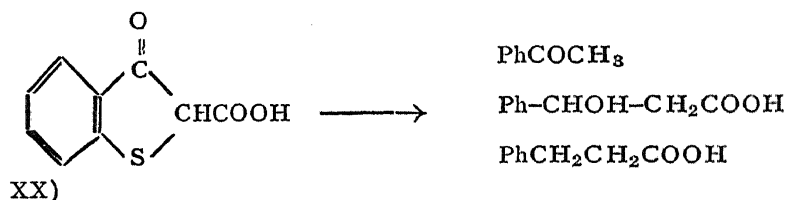


Blicke and Sheets⁷ obtained ethylbenzene by the action of Raney nickel on thionaphthene, thioindoxyl, acetophenone or methyl phenyl carbinol in boiling alcoholic solution. By treatment of thioindoxyl with Raney nickel

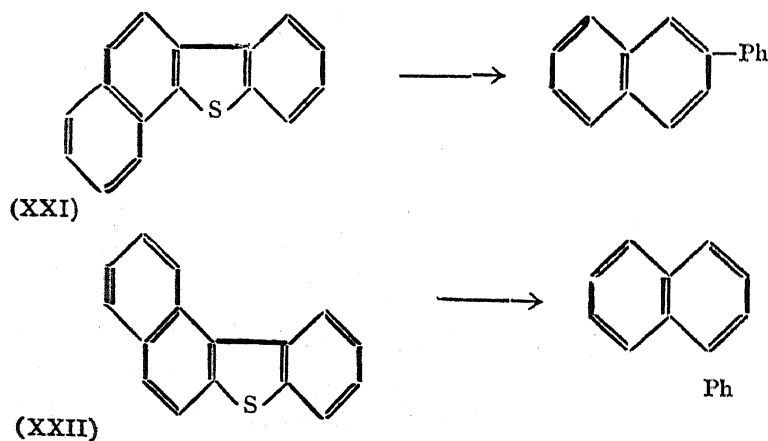
in aqueous sodium hydroxide at 0-5° we have obtained acetophenone in 72% yield. Desulphurization of 3-hydroxythionaphthene-2-carboxylic acid



(thioindoxyllic acid, XX) was next studied under various conditions. Under mild conditions benzoylactic acid was probably formed as the first step in the desulphurization but the major product isolated was always β -phenyl- β -hydroxypropionic acid. β -Phenylpropionic acid and acetophenone in the form of the 2:4-dinitrophenylhydrazone were also isolable. Thioindoxyllic acid was completely desulphurized in 5 minutes by the action of Raney nickel in ice-cold aqueous alkali with the formation of β -phenyl- β -hydroxypropionic acid as the main product.



The constitution of 1:2-benzo-9-thiafluorene (XXI) and 3:4-benzo-9-thiafluorene (XXII), which have been recently reported,⁸ was proved by desulphurization with Raney nickel in alcohol. The former gave 2-phenylnaphthalene and the latter 1-phenylnaphthalene.



EXPERIMENTAL

Reduction of thioindigo (I)

Thioindigo (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered. The filtrate, on removal

of alcohol, gave a liquid which was dissolved in ether and extracted with 5% sodium bicarbonate solution. Removal of ether gave a liquid (2.7 g.) which on distillation (b.p. 140–50°/2 mm.) gave a pink solid, m.p. 45–47° undepressed when mixed with 1 : 4-diphenylbutane (III), obtained in a previous degradation of the dye (see Part II).¹

Oxidation of (III)

A mixture of (III) (0.2 g.) and 5% nitric acid (22.5 c.c.) was heated in a sealed tube at 150–80° for 12 hours. The mixture was extracted with ether. The ether extract was shaken with 5% sodium bicarbonate solution. The bicarbonate extract was acidified and ether extracted. Removal of ether gave a cream coloured product (0.2 g.) which was crystallized from water. A pale yellow solid (0.025 g., m.p. 170–75°), which contained nitrogen, first separated and was filtered off. The mother liquor was concentrated when needles (0.1 g.), m.p. 117–18°, were obtained. Recrystallization from water gave colourless needles, m.p. 122°, undepressed when mixed with benzoic acid.

Reduction of Durindone Orange R (II)

Durindone Orange R (12 g.) was extracted with boiling water and the residue (5 g.) was reduced with Raney nickel (50 g.) in boiling alcohol (500 c.c.) for 7 hours under stirring. The mixture was left overnight and filtered. The filtrate on removal of alcohol gave a sticky product (A) (0.93 g.). The nickel residue was treated with hydrochloric acid, filtered, washed and extracted in a Soxhlet with acetone and benzene. The residue obtained on removal of the solvents was extracted with ether. Removal of ether gave a low melting product (2.4 g.). The mixture of the latter with (A) was distilled at 145–50°/2 mm. and crystallized from alcohol in colourless plates, m.p. 74–76°, raised to 76–77° by recrystallization from the same solvent. It analysed for 1 : 4-bis-*p*-ethoxyphenylbutane (IV) (Found: C, 81.0; H, 8.6. $C_{20}H_{26}O_2$ requires C, 80.5; H, 8.7%).

Oxidation of (IV)

A mixture of (IV) (0.45 g.) and 5% nitric acid (32 c.c.) was heated in a sealed tube at 150–80° for 12 hours. The crude acid, isolated by extraction with aqueous sodium bicarbonate, crystallized from aqueous alcohol in colourless needles, m.p. 195°, undepressed when mixed with *p*-ethoxybenzoic acid.

Reduction of Durindone Red 3BS

Method A.—Durindone Red 3BS was purified by successive extractions with boiling water and 5% boiling hydrochloric acid. The purified dye

(10 g.) was precipitated from a solution in oleum, filtered and washed. The wet cake was vatted with glucose (50 g.) and 10% caustic soda solution (500 c.c.) at 70–80°. The solution was treated with Raney alloy (95 g.) in 10% caustic soda solution (500 c.c.) for 7 hours on a water-bath, left overnight, and filtered. The nickel residue was treated with hydrochloric acid, filtered, washed and extracted with benzene in a Soxhlet. The product (3.6 g.) recovered from the extract, was ether-extracted when an insoluble residue (0.35 g.) was obtained which crystallized from aqueous acetone in colourless plates, m.p. 180–81°. It analysed for 3:3'-dichloro-5:5'-dimethyldiphenacyl (V) (Found: C, 64.6; H, 5.2. $C_{18}H_{16}Cl_2O_2$ requires C, 64.5; H, 4.8%). The ether extract, after removal of the above product, gave an oil (3.2 g.) which was treated with *n*-hexane. A brown product (0.51 g.) separated which crystallized from aqueous acetone in colourless plates, m.p. 113–14°. It analysed for 5-chloro-3:3'-dimethyldiphenacyl (VI) (Found: C, 71.3; H, 6.4. $C_{18}H_{17}ClO_2$ requires C, 71.9; H, 5.6%). The product (2.64 g.), obtained from the hexane solution, was distilled when a pale yellow liquid, b.p. 196–200°/10 mm. was obtained. It analysed for 1:4-bis-*m*-tolyl-1-butanol (VII) (Found: C, 84.4; H, 8.3. $C_{18}H_{22}O$ requires C, 85.0; H, 8.7%). Attempts to isolate pure degradation products from the alkaline solution obtained after removal of nickel were unsuccessful.

Method B.—The commercial dye (6 g., containing 4.5 g. of the pure dye) was vatted with sodium hydrosulphite (6 g.) and 1.5% caustic soda solution (1,000 c.c.) at 85°. Caustic soda (20 g.) was added, followed by Raney alloy (50 g.). The mixture was stirred for 2 hours on a water-bath and filtered. The filtrate, as in Method A, did not yield any pure products. The nickel residue was extracted with benzene as in Method A. The sticky product (2.0 g.), obtained on removal of benzene, was extracted with ether. The ether-insoluble product (0.3 g.) crystallized from alcohol in colourless plates, m.p. 176–78°, undepressed when mixed with (V). The product from the ether solution was treated with *n*-hexane. The hexane-insoluble solid (0.33 g.) was dissolved in benzene and chromatographed on alumina. The major fraction gave colourless plates, m.p. 112–13°, from aqueous acetone, undepressed when mixed with (VI). The hexane-soluble liquid (1.3 g.) on distillation gave a chlorine-free liquid, b.p. 165–70° (Found: C, 83.5; H, 8.1%).

Method C.—The purified dye (5 g.) was reduced with Raney nickel (50 g.) in boiling alcohol (500 c.c.) for 7 hours under stirring and filtered hot. The product obtained from the alcoholic solution was dissolved in ether and extracted with aqueous sodium bicarbonate. Removal of ether gave an oil (2 g.) which was dissolved in benzene, and chromatographed on

alumina. The major zone yielded a product (1.8 g.), which on distillation gave 1:4-di-*m*-tolylbutane (VIII), colourless liquid, b.p. 145–50°/1.5 mm. (Found: C, 90.6; H, 9.4. $C_{18}H_{22}$ requires C, 90.8; H, 9.2%).

Oxidation of (VIII)

A mixture of (VIII) (0.10 g.) and 5% nitric acid (22.5 c.c.) was heated in a sealed tube at 150–80° for 12 hours. The pale yellow product (0.026 g.) crystallized from water in colourless needles, m.p. 332–33°, undepressed when mixed with isophthalic acid.

2:5-Di-(3'-chloro-5'-methyl) phenylfuran (IX)

A mixture of (V) (0.1 g.), glacial acetic acid (5 c.c.) and concentrated hydrochloric acid (5 c.c.) was refluxed for 3 hours and poured over crushed ice. The product which separated was filtered and washed. Crystallization from alcohol gave colourless needles, m.p. 162–63°, of the furan (IX) (Found: C, 67.7; H, 4.7. $C_{18}H_{14}Cl_2O$ requires C, 68.1; H, 4.4%).

Reduction of Durindone Brown GS

Method A.—Durindone Brown GS was extracted with boiling water and boiling 5% hydrochloric acid, filtered, washed and dried. The purified dye (20 g.) was precipitated from concentrated sulphuric acid and the wet cake was treated with Raney alloy (90 g.) in 10% caustic soda solution (900 c.c.) on a water-bath for 1½ hours. The mixture was filtered. The alkaline filtrate did not yield any organic material. The nickel residue was extracted with benzene, and evaporation of the solvent gave a dark coloured product (14.12 g.), which was extracted with ether. The ether-insoluble solid (5.61 g.) crystallized from alcohol in colourless plates, m.p. 141–42°, undepressed when mixed with 1:2-di- α -naphthoylethane (XI), prepared according to Lutz *et al.*⁹ The ether extract after separation of the above product gave an oil (8.51 g.), which was distilled. The fraction boiling at 140–42°/12 mm. was a yellow liquid which analysed for 1:4-di- α -tetralylbutane (XII) (Found: C, 90.3; H, 9.3. $C_{24}H_{30}$ requires C, 90.6; H, 9.4%).

Method B.—The purified dye (5 g.) was treated with Raney nickel in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. Removal of alcohol gave an oil (2.0 g.), which was dissolved in benzene and chromatographed on alumina. The major zone gave a product (1.9 g.), which distilled as a colourless liquid, b.p. 215–20°/1 mm., having a blue fluorescence in ultraviolet light and analysing for 1:4-di- α -tetralylbutane (XII) (Found: C, 90.0; H, 9.0. $C_{24}H_{30}$ requires C, 90.6; H, 9.4%).

2:5-Di- α -naphthylfuran (XIII)

A mixture of (XI) (0.2 g.), glacial acetic acid (5 c.c.) and concentrated hydrochloric acid (8 c.c.) was refluxed for 6½ hours and added to crushed ice. Crystallization of the product from alcohol gave colourless plates, m.p. 85–86°, which analysed for the furan (XIII) (Found: C, 89.4; H, 5.0. $C_{24}H_{16}O$ requires C, 90.0; H, 5.0%).

Reduction of Ciba Brown 2R

Ciba Brown 2R was purified by successive extractions with boiling water and with 5% boiling hydrochloric acid, filtered, washed and dried. Three crystallizations from *o*-dichlorobenzene gave brown needles, which did not contain chlorine or nitrogen (Found: S, 16.1. Calc. for $C_{24}H_{12}O_2S_2$: S, 16.2%).

Method A.—The purified dye (5 g.) was precipitated from concentrated sulphuric acid and the wet cake was treated with Raney alloy (27.5 g.) in 10% caustic soda solution (275 c.c.) for 5 hours on a water-bath. The mixture was filtered and the nickel residue extracted with benzene as usual. On cooling the benzene extract (300 c.c.), a substance (0.1 g.) separated which crystallised from benzene in colourless plates, m.p. 213–14° (Found: C, 83.5; H, 6.7. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.2%). The stated theoretical figures for C and H are for 1:4-di- α -naphthyl-1:4-butanediol (XIV). The benzene mother liquor was concentrated to 20 c.c. and cooled, when a colourless substance (0.61 g.) separated, which crystallized from alcohol in colourless plates, m.p. 139–40°, undepressed when mixed with (XI). The benzene mother liquor on removal of the solvent gave an oil (2.3 g.), which after repeated distillation, gave a colourless liquid, b.p. 225°/7–8 mm., showing a blue fluorescence in ultraviolet light (Found: C, 90.2; H, 9.0. $C_{20}H_{30}$ requires C, 90.6; H, 9.4%). The required C, H values are for 1:4-di- α -tetralylbutane (XII).

Method B.—The purified dye (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. The filtrate on removal of alcohol gave an oil (1.84 g.), which was dissolved in benzene and chromatographed on a column of alumina. The major zone gave a product (1.7 g.) which distilled as a colourless liquid, b.p. 220–25°/1 mm., exhibiting a blue fluorescence in ultraviolet light, and analysing for 1:4-di- α -tetralylbutane (XII) (Found: C, 90.1; H, 9.2. $C_{24}H_{30}$ requires C, 90.6; H, 9.4%).

Reduction of 2:3'-bis-thionaphthene-indigo (XV)

Method A.—2:3'-Bis-thionaphthene-indigo (5 g.) was treated with Raney alloy (22.5 g.) in 10% caustic soda solution (225 c.c.) for 2 hours on a water-

bath and the mixture filtered. The nickel residue was extracted with benzene as usual, and the oil (1.0 g.) obtained was dissolved in benzene and chromatographed on a column of alumina. The major zone led to a yellow liquid (0.4 g.), b.p. 165–70°/7 mm., having a bluish violet fluorescence and analysing for 2:4-diphenyl-1-butanol (XVI) (Found: C, 85.2; H, 8.4. $C_{16}H_{18}O$ requires C, 85.0; H, 8.0%).

Method B.—2:3'-Bis-thionaphthene-indigo (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. The filtrate, on removal of alcohol, gave a red, bicarbonate-insoluble liquid (2.7 g.) which was dissolved in benzene and chromatographed on alumina. The major zone gave a colourless liquid (1.7 g.), b.p. 105–10°/1 mm., which analysed for 1:3-diphenylbutane (XVII), prepared earlier by Stobbe and Posnjak¹⁰ (Found: C, 91.3; H, 8.7. Calc. for $C_{16}H_{18}$: C, 91.4; H, 8.6%).

Reduction of Ciba Scarlet G

Ciba Scarlet G was purified by successive extraction with boiling water and boiling 5% hydrochloric acid. The purified dye crystallized from benzene in scarlet needles, m.p. 269–70° (Found: S, 9.9. Calc. for $C_{20}H_{10}O_2S$: S, 10.2%).

Method A.—The purified dye (10 g.) was precipitated from concentrated sulphuric acid and the wet cake was treated with Raney alloy (45 g.) in 10% aqueous caustic soda solution (450 c.c.) for 90 minutes on a water-bath and filtered. The nickel residue was treated as usual and extracted with alcohol. The product (8.86 g.) obtained from the alcoholic extract was dissolved in carbon tetrachloride and chromatographed on alumina, when it separated into 6 zones. The major zone yielded a thick brown liquid which was re-chromatographed, when it again separated into 5 zones. The major zone gave a pale yellow liquid, b.p. 170–75°/5 mm. which analysed for (XVIII) (Found: C, 87.5; H, 7.2. $C_{20}H_{20}O$ requires C, 87.0; H, 7.2%). It gave a 2:4-dinitrophenylhydrazone which could not however be crystallised.

Method B.—The purified dye (5 g.) was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 7 hours and filtered hot. The product (2.9 g.) obtained on removal of alcohol was dissolved in benzene and chromatographed on alumina. The major zone gave a yellow oil (2.7 g.), b.p. 168–72°/1 mm., analysing for (XIX) (Found: C, 89.3; H, 9.4. $C_{20}H_{28}$ requires C, 89.6; H, 10.4%).

Reduction of thioindoxyl

"Thioindoxyl melt" (I.C.I., 40 g.) was dissolved in cold water (200 c.c.), the solution treated with norit and filtered. The filtrate was cooled and acidified by cold dilute sulphuric acid. The precipitate of 3-hydroxythionaphthene-2-carboxylic acid (XX) was suspended in water and made alkaline to Brilliant Yellow paper by addition of 5% caustic soda solution. The solution was stirred on a water-bath at 60–70° to effect decarboxylation of thioindoxylic acid (XX). After the decarboxylation was complete (30 minutes) the mixture was made alkaline (phenolphthalein), treated with norit and filtered. The alkaline solution was cooled and acidified. The very pale pink precipitate of thioindoxyl was washed with cold water and dried in a vacuum. The substance (7.7 g.) was treated with Raney nickel (50 g.) in 10% caustic soda solution (250 c.c.) at 0–5° for 90 minutes and filtered. The alkaline filtrate was extracted with ether. The ether extract on removal of the solvent gave an oil (4.43 g.). Fractionation yielded a colourless liquid, b.p. 202–3°. It formed a 2:4-dinitrophenylhydrazone, m.p. 236–37° (*dec.*) undepressed when mixed with acetophenone dinitrophenylhydrazone.

Reduction of thioindoxylic acid (XX)

Method A.—Thioindoxylic acid (5 g.), prepared as above from thioindoxyl melt (20 g.), was treated with Raney nickel (50 g.) in boiling alcohol (500 c.c.) under stirring for 9 hours and filtered hot. The alcoholic filtrate, on removal of solvent, gave a liquid (1.6 g.) which was extracted with 10% sodium bicarbonate solution. The bicarbonate-insoluble liquid (0.34 g.) distilled at 100–40°, and it did not give a dinitrophenylhydrazone. The bicarbonate solution, on acidification and ether extraction, gave a liquid (1.2 g.). This was extracted with petroleum ether (b.p. 65–75°), when a solid (0.19 g.), m.p. 84–6°, separated, which crystallized from benzene in colourless prisms, m.p. 92°, undepressed when mixed with β -phenyl- β -hydroxypropionic acid. The petroleum ether solution on concentration and cooling gave colourless prisms, m.p. 46–7°, undepressed when mixed with β -phenylpropionic acid.

Method B.—Thioindoxylic acid (5 g.) was treated for 5 minutes with Raney nickel (50 g.) and 3% caustic soda solution (150 c.c.) in an ice-bath under stirring, and the mixture filtered. The filtrate on ether extraction did not yield any alkali-insoluble product. The alkaline solution was cooled and made slightly acidic with cold dilute hydrochloric acid, and ether extracted. The extract on removal of ether in a current of dry air gave an orange-coloured liquid. On trituration with petroleum ether a solid (2.0 g.)

separated, which crystallized from benzene in colourless prisms, m.p. 92°, undepressed when mixed with β -phenyl- β -hydroxypropionic acid. The petroleum ether solution, on removal of solvent, yielded a sticky substance (1.1 g.), which contained acetophenone identified as the 2:4-dinitrophenylhydrazone.

Reduction of 1:2-benzo-9-thiafluorene (XXI)

A mixture of (XXI) (0.8 g.), Raney nickel (8 g.) and alcohol (100 c.c.) was refluxed under stirring for 2½ hours and filtered hot. Removal of alcohol from the filtrate gave a sticky substance (0.68 g.). It was distilled at 130–50°/0.7 mm., when a colourless liquid distillate was obtained which soon solidified. Crystallization from alcohol gave colourless plates, m.p. 100–1°, undepressed when mixed with 2-phenylnaphthalene prepared according to Hey *et al.*¹¹

Reduction of 3:4-benzo-9-thiafluorene (XXII)

A mixture of (XXII) (0.8 g.), Raney nickel (8 g.) and alcohol (100 c.c.) was refluxed under stirring for 3½ hours and filtered hot. The alcoholic filtrate on removal of solvent gave a red liquid (0.57 g.). The fluorescent solution in benzene was chromatographed on alumina in ultraviolet light. The major zone gave an orange liquid (0.47 g.), which distilled at 135–40°/1 mm. to a colourless liquid with a blue fluorescence (Found: C, 93.7; H, 6.4. Calc. for C₁₆H₁₂: C, 94.1; H, 5.9%). The absorption spectrum was identical with that of 1-phenylnaphthalene.¹²

SUMMARY

Desulphurization of the following thioindigoid dyes has been studied: Durindone Red B, Durindone Orange R, Durindone Red 3BS, Durindone Brown GS, Ciba Brown 2R and Ciba Scarlet G. The action of Raney alloy in aqueous alkali gave diphenacyl derivatives in most cases together with further reduction products, such as 1:4-diaryl-1:4-butanediols and 1:4-diaryl-1-butanol. Reduction of the dyes with Raney nickel in alcohol gave 1:4-diarylbutanes as the major products. The chlorine atoms in Durindone Red 3BS were partially or completely removed during the reduction. The constitution of Ciba Brown 2R was proved by reduction and the dye was shown to be identical with Durindone Brown GS. The constitution of the diphenacyls was proved by conversion to 1:4-diarylfurans and by synthesis. The constitution of 1:4-diarylbutanes was proved by oxidation to the corresponding benzoic acids. Reduction of 2:3'-bis-thionaphthene-indigo gave an alcohol, probably constituted as 2:4-diphenyl-1-butanol.

Mild reduction of thioindoxyl gave acetophenone, thioindoxylic acid gave β -phenyl- β -hydroxypropionic acid, together with dihydrocinnamic acid.

The constitution assigned earlier to 1:2-benzo- and 3:4-benzo-9-thiafluorenes was confirmed by their desulphurization to β - and α -phenylnaphthalene respectively by means of Raney nickel.

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