705. *New Intermediates and Dyes. Part VI.* The Chemistry of 2-n-Butylanthraquinone. Derived Dyes for Synthetic Fibres.*

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Many derivatives of 2-*n*-butylanthraquinone have been prepared and orientated.

The nitro-group in 2-*n*-butyl-1-nitroanthraquinone has been replaced, to give a series of alkylamino- and arylamino-derivatives, which are dyes for cellulose acetate rayon, Nylon, and Terylene; apart from a slight bathochromic effect, especially on Nylon, the shades and fastness of the dyeings were only slightly affected by the butyl group.

Dinitration of 2-*n*-butylanthraquinone was investigated in detail; the derived 1 : 5- and 1 : 8-diamino- and -bismethylamino-quinones were compared with the bluer 1 : 4-disubstituted analogues, prepared from 1-amino- and 1-methylamino-4-bromo-2-*n*-butylanthraquinone, respectively.

THIS paper concerns 2-*n*-butylanthraquinone, particularly dyes obtained by the introduction of the group NHR into position 1.

During the cyclisation of pure 2-4′-*n*-butylbenzoylbenzoic acid to 2-*n*-butylanthraquinone, achieved in 74% yield, by Peters and Rowe's method,[1] the butyl group was eliminated to a small extent, *ca.* 4% of anthraquinone being isolated. In experiments with the *tert.*-butyl analogues, the 2-*tert.*-butylanthraquinone was accompanied by 4—5% of anthraquinone. Elimination of the butyl group occurred during cyclisation rather than in the Friedel–Crafts reactions. 2-4′-Methylbenzoylbenzoic acid, however, similarly gave 2-methylanthraquinone, and no anthraquinone. Elimination of an alkyl group is unusual in such reactions, though Fieser and Peters [2] record the elimination of the 4- and the 4′-methyl group during the pyrolysis–cyclisation of 4 : 4′-dimethyl-1 : 1′-dinaphthyl ketone, and Ipatieff and Carson [3] describe dealkylation of di-*tert.*-butylbenzene to *tert.*-butylbenzene by sulphuric acid at 15°.

In reactions with alkyl derivatives, rearrangement, migration, and disproportionation are well known; in the Friedel–Crafts reaction *sec.*-butylbenzene and phthalic anhydride gave only a resinous 2-4′-*sec.*-butylbenzoylbenzoic acid, and difficulties in the purification of 2-4′-*n*-butylbenzoylbenzoic acid may be due to slight isomerisation by aluminium chloride.

2-*n*-Butylanthraquinone was mononitrated by Moualim and Peters's method,[4] but appreciable dinitration occurred also; the use of nitric acid in 100% sulphuric acid at $<35°$ gave 65% of 2-*n*-butyl-1-nitroanthraquinone, with negligible dinitration. This product was orientated on oxidation with acid dichromate to 1-nitroanthraquinone-2-carboxylic acid, identical with that prepared from 2-methyl-1-nitroanthraquinone. Further evidence of the α-position of the nitro-group was afforded by conversion of the compound by aqueous-alcoholic ammonia at 130° into 1-amino-2-*n*-butylanthraquinone, best prepared however by reduction with aqueous-alcoholic sodium sulphide.

The bright yellow 1-acetamido- and golden-yellow 1-benzamido-2-*n*-butylanthraquinone were purified by chromatography; the latter dyed cotton from an alkaline sodium dithionite vat a pale greenish-yellow.

1-Amino-2-*n*-butylanthraquinone was converted by the diazo-reaction into 2-*n*-butyl-1-chloroanthraquinone, identical with one of the products obtained by direct controlled chlorination of 2-*n*-butylanthraquinone by sulphuryl chloride in nitrobenzene; further,

* Part V, *J.*, 1957, 1525.

[1] Peters and Rowe, *J.*, 1945, 181.
[2] Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 3742.
[3] Ipatieff and Carson, *ibid.*, 1937, **59**, 1417.
[4] Moualim and Peters, *J.*, 1948, 1627.

the 1-chloro-derivative was reconverted into 1-amino-2-*n*-butylanthraquinone by acid hydrolysis of the derived 2-*n*-butyl-1-toluene-*p*-sulphonamidoanthraquinone.

Pure 2-*n*-butyl-1-nitroanthraquinone with the appropriate *n*-alkylamine in alcohol at 120—125° gave the deep bordeaux 2-butyl-1-methylamino-, -1-ethylamino-, -1-*n*-propylamino-, and -1-*n*-butylamino-anthraquinone in yields of 80—83%.

The orange 2-*n*-butyl-1 : 2′ : 2′-difluoroethylaminoanthraquinone was prepared from the nitro-compound in boiling dry pyridine, but better by heating it with 2 : 2-difluoroethylamine, sodium acetate, copper acetate, and alcohol at 140—150°. An analogous derivative could not be obtained from 2 : 2 : 2-trifluoroethylamine.

1-Amino-2-*n*-butylanthraquinone was mainly unchanged on attempted reaction with ethylene chlorohydrin at 125—130°, but the deep purple 2-*n*-butyl-1-2′-hydroxyethylaminoanthraquinone was obtained from the 1-nitro-derivative and alcoholic 2-hydroxyethylamine at 120—125°, or less readily in refluxing pyridine in presence of sodium acetate, copper acetate, and a trace of copper bronze. In these reactions, particularly in open reflux, the use of an excess of 2-hydroxyethylamine gave a considerable amount of 1-amino-2-*n*-butylanthraquinone, formed by decomposition of 2-hydroxyethylamine. As the 1-2′-hydroxyethylamino-derivative was strongly absorbed on alumina, the 1-amino-derivative was readily separated. Meltsner *et al.*[5] observed that when nitrobenzene was heated with 2-hydroxyethylamine and sodium carbonate, 12% of aniline was formed, the 2-hydroxyethylamine being partly decomposed to ammonia and acetaldehyde.

Refluxing at 1 atm. was effective in the interaction of *cyclo*hexylamine and 2-butyl-1-nitroanthraquinone, which in boiling pyridine afforded the dark red 1-*cyclo*hexylamino-2-*n*-butylanthraquinone; similarly, refluxing with benzylamine in presence of sodium acetate and copper acetate gave 90% of the bright red 1-benzylamino-derivative. The bordeaux 1-anilino-2-*n*-butylanthraquinone was obtained in 50% yield by use of refluxing aniline in presence of copper bronze.

Certain of the above 1-substituted 2-*n*-butylanthraquinones were tested as dyes and compared with the respective anthraquinone analogues. In general, introducing the *n*-butyl group reduced the rate of dyeing at ordinary dyeing temperatures on cellulose acetate rayon and Nylon; on Terylene, differences were slight. Apart from a slight bathochromic effect, especially on Nylon, the shades of all dyeings were similar to those shown by the analogues containing no butyl group. Fastness to sublimation, light, and burnt gas fumes was not improved by the presence of the butyl group, but fastness to washing was excellent on all three fibres, possibly owing to increased molecular size. The alkylamino-group was bathochromic in the order: anilino > 2-hydroxyethylamino > amino > 2 : 2-difluoroethylamino. With cellulose acetate rayon and Nylon, the rate of dyeing was of the order amino = 2-hydroxyethylamino > 2 : 2-difluoroethylamino anilino; on Terylene, dyeings gave almost complete exhaustion of the dyebath.

Further evidence that the orientation of 1-amino-2-*n*-butylanthraquinone was correc was afforded by its monobromination, followed by replacement of the bromine by the amino-group. Thus, bromination in dry nitrobenzene at 95° yielded 60% of 1-amino-4-bromo-2-*n*-butylanthraquinone; the melting point, as with certain other anthraquinone derivatives, is not an absolute criterion of purity, and confirmatory analyses from successive crystallisations were carried out to ensure purity; chromatography was unsuccessful. The bromine atom was readily replaced, to give the deep violet 1 : 4-diamino-2-*n*-butylanthraquinone, which gave similar dyeings to those from 1 : 4-diaminoanthraquinone. The derived yellow diacetamido- and the golden-orange dibenzamido-compound were shown to be homogeneous by chromatography. 4-Bromo-2-*n*-butyl-1-methylaminoanthraquinone, obtained by bromination of 2-*n*-butyl-1-methylaminoanthraquinone, and alcoholic methylamine yielded the deep violet 1 : 4-bismethylamino-2-*n*-butylanthraquinone.

Dinitration of 2-*n*-butylanthraquinone was studied in detail, and chromatography and

[5] Meltsner, Wohlberg, and Kleiner, *J. Amer. Chem. Soc.*, 1935, **57**, 2554.

fractional crystallisation were employed in the separation of the dinitro- and the derived diamino-derivatives. Potassium nitrate and sulphuric acid at <40° afforded approximately 55·6% of 1 : 5- and 33·3% of 1 : 8-, with 5·8% of 1 : *x*-dinitro-compound, and 5·2% of 2-*n*-butyl-1-nitroanthraquinone (yields are based on relative amounts of pure products isolated). Reduction by aqueous-alcoholic sodium sulphide of the various fractions gave 1 : 5- and 1 : 8-diamino-2-*n*-butylanthraquinone, and the 1 : *x*-diamino-derivative was separated by chromatography into two diamines, which were probably the 1 : 6- and 1 : 7-compounds. Diacetylation and dibenzoylation of the 1 : 5-diamine, as expected, proceeded more readily than with the 1 : 8-diamine.

The reddish-brown 2-*n*-butyl-1 : 5- and -1 : 8-bismethylaminoanthraquinone were prepared from the respective dinitro-analogues by the usual procedure. When 2-*n*-butyl-1 : 5-dinitroanthraquinone was heated with freshly distilled 2-hydroxyethylamine at 135—140° in presence of sodium acetate and alcohol, and the products were chromatographed, the reddish-violet 1(or 5)-amino-2-*n*-butyl-5(or 1)-2′-hydroxyethylamino- and the magenta 2-butyl-1 : 5-di-2′-hydroxyethylaminoanthraquinone were isolated. Isolation of the monoamine parallels the reaction recorded with ethanolamine.

On cellulose acetate rayon, dyeings of the three diamino-2-*n*-butylanthraquinones showed the deep reddish-violet of the 1 : 4-diamine, the 1 : 5- and 1 : 8-diamines affording reddish-orange and orange-red shades, respectively. Replacement of the amino-group by methylamino showed a bathochromic effect in all cases, the 1 : 4-, 1 : 5-, and 1 : 8-derivatives giving blue, bluish-red, and reddish-violet shades, respectively.

Experimental

2-n-*Butylanthraquinone*.—Cyclisation [1] of pure 2-4′-*n*-butylbenzoylbenzoic acid (10 g.), m. p. 100°, gave 2-*n*-butylanthraquinone, cream needles, m. p. 90° (6·9 g., 74%). Fractional crystallisation of the cyclised product yielded anthraquinone, pale yellow needles, m. p. and mixed m. p. 286° (from acetic acid) (0·3 g., 4%). Fractionation of the product derived from pure 2-*n*-butylanthraquinone and 20% oleum at 90—95° for 1 hr. gave no anthraquinone; only unchanged product was isolated, but there was some charring and sulphonation.

Interaction of *sec.*-butylbenzene, b. p. 173°, with phthalic anhydride in carbon disulphide or *s*-tetrachloroethane, was investigated several times, but yielded only an alkali-soluble yellow glass. Treatment with 20% oleum at 95° afforded a dark resin, with sulphonated products.

2-n-*Butyl*-1-*nitroanthraquinone*.—(*a*) Nitration of 2-*n*-butylanthraquinone (13·2 g.) by Moualim and Peters's method [4] gave 2-*n*-butyl-1 : 5-dinitroanthraquinone (2·3 g.), pale yellow needles, m. p. 264—265° (Found: C, 60·95; H, 4·0; N, 8·0. Calc. for $C_{18}H_{14}O_6N_2$: C, 61·0; H, 4·0; N, 7·9%), and 2-*n*-butyl-1-nitroanthraquinone, pale yellow needles, m. p. 150° (9·4 g., 60·8%) (Found: C, 69·7; H, 4·9; N, 4·5. Calc. for $C_{18}H_{15}O_4N$: C, 69·9; H, 4·9; N, 4·5%). Reaction for 10—12 min. at >38° gave some unnitrated material and the 1-nitro-derivative (7·8 g.), with only a small amount of dinitro-derivative.

(*b*) 2-*n*-Butylanthraquinone (6·3 g., 1 mol.) in 100% sulphuric acid (25 ml.) was stirred at 20° during the addition of nitric acid (*d* 1·41; 2·3 g., 1·08 mols.) and 100% sulphuric acid (6 ml.) (30 min.) at <35°. After 75 minutes' stirring at room temperature addition to water gave a pale yellow solid (6·9 g.), m. p. 125—130°, and thence by crystallisation from acetic acid the 1-nitro-derivative (4·8 g., 65%), m. p. 150°.

Oxidation of 2-n-*Butyl*-1-*nitroanthraquinone*.—Sodium dichromate (3·2 g.) in water (4 ml.) was added during 30 min. to the 1-nitro-derivative (3·7 g.) and 75% aqueous sulphuric acid (8 ml.) at 50°. After 20 hours' stirring at 65°, cooling, and filtration, the solid product was washed with water and digested with 20% aqueous sodium hydroxide at 85—90° for 45 min.; the purple alkaline filtrate was acidified with dilute sulphuric acid, to yield a gelatinous brownish-yellow precipitate, m. p. 260—270°. Four crystallisations (charcoal) from ethanol afforded pale brownish-yellow leaflets (0·2 g.), m. p. 289—290°, not depressed on admixture with 1-nitroanthraquinone-2-carboxylic acid, m. p. 290°, prepared from 2-methyl-1-nitroanthraquinone.

1-*Amino*-2-n-*butylanthraquinone*.—The 1-nitro-derivative (7 g.), prepared by method (*b*), was reduced by aqueous-alcoholic sodium sulphide [4] to the amine, long red needles, m. p. 175—176° (lit.,[4] m. p. 172°). Conversion of the nitro- into the amino-compound was also effected by heating it with aqueous ammonia (*d* 0·88; 18 ml. per g.) at 130° for 4 hr. It gave a stable diazonium salt, precipitated by zinc chloride as the double salt from the hydrochloric acid solution.

The free amine dyed cellulose acetate rayon and Nylon orange and salmon-pink shades, respectively.

The acetyl derivative crystallised from acetic acid in yellow needles, m. p. 154° (lit.,[4] m. p. 140°); further crystallisations did not alter the m. p., but chromatography from benzene on alumina gave a main yellow zone yielding yellow needles (from ethanol), m. p. 197°, of the 1-acetamido-derivative (Found: C, 74·9; H, 6·1; N, 4·3. Calc. for $C_{20}H_{19}O_3N$: C, 74·75; H, 6·0; N, 4·4%). Heating the amine and benzoyl chloride in dry nitrobenzene at 140—145° for 45 min. and then removing nitrobenzene with steam afforded a solid which crystallised from alcohol in golden-yellow needles, m. p. 128—129°. Chromatography (benzene–alumina) yielded similar needles, m. p. 129°, of 1-*benzamido*-2-n-*butylanthraquinone* (Found: C, 78·1; H, 5·5; N, 3·7. $C_{25}H_{21}O_3N$ requires C, 78·3; H, 5·5; N, 3·65%).

2-n-*Butyl*-1-*chloroanthraquinone*.—(*a*) 1-Amino-2-*n*-butylanthraquinone (2 g., 1 mol.) was dissolved in hot acetic acid (24 ml.), and the solution cooled rapidly to room temperature and added gradually to sodium nitrite (0·55 g., 1·1 mols.) in concentrated sulphuric acid (4 ml.). After 10 min., the resulting solution was added slowly to a stirred hydrochloric acid solution of cuprous chloride (freshly prepared from 2·5 g. of hydrated copper sulphate) at room temperature. After 1 hr., the mixture was warmed at 60° until evolution of nitrogen had ceased, and the resulting solid was collected and crystallised from ethanol in pale orange-brown prisms, m. p. 95—98° (1·9 g., 88·8%). Chromatography (benzene–alumina) gave a main yellow zone which afforded pale cream prisms, m. p. 103—104° (from ethanol), of the 1-*chloro-derivative* (Found: C, 72·2; H, 5·2; Cl, 11·75. $C_{18}H_{15}O_2Cl$ requires C, 72·4; H, 5·1; Cl, 11·9%).

(*b*) 2-*n*-Butylanthraquinone (4 g.) in dry nitrobenzene (10 ml.) was refluxed on the steam-bath with sulphuryl chloride (4·2 g.) and iodine (0·4 g.), for periods varying from 5 to 15 hr. Nitrobenzene was removed with steam, and the resulting solid was fractionally crystallised from ethanol. The products, usually cream solids, were as follows: reaction time, 5 hr., m. p. 74° (Found: Cl, 4·15%) and m. p. 80° (Found: Cl, 4·5%); 7 hr., m. p. 90° (Cl, 7·5%); 10 hr., m. p. 95—97° (Cl, 13·4%) and m. p. 102° (Cl, 11·65%); 12 hr., m. p. 108° (Cl, 14·45%) and m. p. 68° (Cl, 12·4%). The purest sample was obtained after reaction for 9 hr., and chromatography from benzene on alumina gave a main yellow zone and thence (from ethanol) cream prisms (0·8 g.), m. p. 103—104° (Found: C, 72·1; H, 4·9; Cl, 11·6%), identical with the product formed by method (*a*).

2-n-*Butyl*-1-*toluene*-p-*sulphonamidoanthraquinone*.—2-*n*-Butyl-1-chloroanthraquinone (1·1 g.) was heated with toluene-*p*-sulphonamide (0·9 g.), fused potassium acetate (0·8 g.), and a crystal of cupric acetate in dry nitrobenzene (10 ml.) at 190° for 3 hr. Most (0·64 g.) of the product was isolated by addition of ethanol; removal of nitrobenzene with steam gave a further 0·2 g. Purification (benzene–alumina) gave a reddish-blue band, rapidly eluted, and a main orange-brown zone; extraction of the latter with ethanol and crystallisation from the same solvent gave brownish-orange needles, m. p. 157°, of the *toluene*-p-*sulphonamido-derivative* (0·51 g.) (Found: C, 68·95; H, 5·25; N, 3·1; S, 7·4. $C_{25}H_{23}O_4NS$ requires C, 69·2; H, 5·35; N, 3·2; S, 7·4%). Hydrolysis of this derivative (0·6 g.) with concentrated sulphuric acid (5 ml.) at 90° for 20 min. afforded 1-amino-2-*n*-butylanthraquinone (0·3 g.), m. p. and mixed m. p. 174—175°.

1-n-*Alkylamino*-2-n-*butylanthraquinones*.—2-*n*-Butyl-1-nitroanthraquinone (1 g.) was heated with the appropriate 33% alcoholic alkylamine (12 ml.) at 120—125° for 2 hr.; the products, purified by chromatography and crystallised from alcohol, were: 2-n-*butyl*-1-*methylamino*- (0·76 g., 80·2%), dark bordeaux needles with a metallic lustre, m. p. 68—69° (Found: C, 77·9; H, 6·5; N, 4·9. $C_{19}H_{19}O_2N$ requires C, 77·8; H, 6·5; N, 4·8%), -1-*ethylamino*- (0·8 g., 80%), red needles, m. p. 85—86° (Found: C, 78·2; H, 7·1; N, 4·6. $C_{20}H_{21}O_2N$ requires C, 78·1; H, 6·9; N, 4·6%), -1-n-*propylamino*- (0·85 g., 81·7%), deep bordeaux needles, m. p. 52—53° (Found: C, 78·7; H, 7·3; N, 4·4. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·2; N, 4·4%), and -1-n-*butylamino*-*anthraquinone* (0·9 g., 83%), deep bordeaux needles, m. p. 51—52° (Found: C, 78·7; H, 7·5; N, 4·15. $C_{22}H_{25}O_2N$ requires C, 78·8; H, 7·5; N, 4·2%). The m. p.s of these derivatives were rather low for effective dyeing procedures.

2-n-*Butyl*-1-2′ : 2′-*difluoroethylaminoanthraquinone*.—(*a*) 2 : 2-Difluoroethylamine (0·8 g.) was added dropwise during 15 min. to a solution of 2-*n*-butyl-1-nitroanthraquinone (1·5 g.) in pure dry pyridine (17 ml.) at 100°, and the mixture then refluxed for 40 hr.; the blood-red mixture was concentrated to 12 ml., then added to water, and the solid (1·35 g.), m. p. 127—129°, was purified by chromatography (toluene–alumina). A small strongly adsorbed reddish-violet zone was noted above the principal reddish-orange zone; the former yielded unidentified reddish-orange prisms (0·04 g.), m. p. 112° (from ethanol) (Found: N, 4·1%), and the latter afforded pale reddish-orange needles (0·6 g.), m. p. 103—104° (alcohol) (Found: C, 69·9; H, 5·4; N, 4·2. $C_{20}H_{19}O_2NF_2$ requires C, 69·95; H, 5·6; N, 4·1%), of the *difluoro-derivative*.

(*b*) The 1-nitro-derivative (1·2 g.), 2 : 2-difluoroethylamine (1·5 g.), fused sodium acetate (1 g.), copper acetate (0·1 g.), and alcohol (10 ml.) at 140—150° for 20 hr. gave a dark reddish-orange product (1·15 g.). Dissolution in chlorobenzene and chromatography on alumina gave (i) (strongly adsorbed) dark orange irregular prisms (0·18 g.), m. p. 118—119° (Found: C, 69·85; H, 5·7; N, 7·25%), of unknown constitution, (ii) (less strongly absorbed) deep red needles (0·4 g.) of 1-amino-2-*n*-butylanthraquinone, m. p. and mixed m. p. 175—176°, and (iii) (eluted) orange needles (0·28 g.), m. p. 103—104° (from ethanol), identical with the product obtained by method (*a*) (Found: C, 70·2; H, 5·9; N, 4·0%).

Reaction with 2 : 2 : 2-*Trifluoroethylamine*.—This amine (2 g.) and 2-*n*-butyl-1-nitroanthraquinone (1 g.), in presence of sodium acetate (0·75 g.) and alcohol (3 ml.) at 140—150° for 15 hr. afforded, after chromatography, a *substance* (dark reddish-orange needles; 0·08 g.), m. p. 144—146° (from ethanol) (Found: C, 66·45; H, 5·15; N, 8·25. $C_{20}H_{18}O_2NF_3$ requires C, 66·5; H, 5·0; N, 3·8%), of unknown constitution, and pale orange needles (0·67 g.), m. p. 145—146°, of unchanged nitro-compound (Found: C, 69·6; H, 4·7; N, 4·8%).

2-n-*Butyl*-1-2′-*hydroxyethylaminoanthraquinone*.—Interaction of 1-amino-2-*n*-butylanthraquinone with ethylene chlorohydrin in presence of sodium and copper acetates in a sealed tube at 125—130° for 3 hr. gave only a trace of bluish-red product, and the amine was mainly recovered. 2-*n*-Butyl-1-nitroanthraquinone (1 g.) and 33% v/v alcoholic 2-hydroxyethylamine at 120—125° for 2 hr. gave, after chromatography (toluene–alumina), red needles (0·2 g.), m. p. 175—176°, of 1-amino-2-*n*-butylanthraquinone; a strongly adsorbed small red zone gave bordeaux prisms (0·25 g.), m. p. 103—104° (from ethanol) (Found: C, 73·5; H, 6·8; N, 3·8. $C_{20}H_{21}O_3N$ requires C, 74·3; H, 6·55; N, 4·3%), of impure product. The use of 2-hydroxyethylamine (5 ml.) and ethanol (6 ml.), as above, again gave a little 1-amino-2-*n*-butylanthraquinone, but the principal dark red zone yielded deep purple prisms (0·4 g., 38%), m. p. 114° [from alcohol–light petroleum (b. p. 60—80°)], of 2-n-*butyl*-1-2′-*hydroxyethylaminoanthraquinone* (Found: C, 74·1; H, 6·4; N, 4·3%). The same product (0·32 g., 30·6%) and 1-amino-2-*n*-butylanthraquinone (0·22 g., 24·3%) were obtained by refluxing the 1-nitro-compound (1 g.) with pyridine (12 ml.) and freshly distilled ethanolamine (0·3 g.) in presence of sodium acetate (0·8 g.), copper acetate (0·1 g.), and a trace of copper bronze. 2-*n*-Butyl-1-2′-hydroxyethylaminoanthraquinone dyed cellulose acetate rayon, Nylon, and Terylene clear pink, bluish-pink, and pink shades, respectively, and all cases showed a slightly bluer shade than the corresponding dyeings from 1-2′-hydroxyethylanthraquinone.

2-n-*Butyl*-1-cyclo*hexylaminoanthraquinone*.—Refluxing 2-*n*-butyl-1-nitroanthraquinone (1 g.) with *cyclo*hexylamine (6 ml.) and dry pyridine (14 ml.) for 7 hr., then adding the mixture to dilute hydrochloric acid gave a resin which on prolonged storage *in vacuo* yielded a dark purple mass (0·78 g.), m. p. 70—75°; ether-extraction of the aqueous layer gave a dark red solid (0·24 g.), m. p. 75—77°. The products were combined and chromatographed (benzene–alumina) to yield a main bright bluish-red zone; extraction with ethanol, followed by crystallisation from light petroleum (b. p. 60—80°), gave dark red needles, m. p. 84—85°, of the 1-cyclo*hexylamino-derivative* (0·75 g., 64·1%) (Found: C, 79·6; H, 7·5; N, 3·7. $C_{24}H_{27}O_2N$ requires C, 79·8; H, 7·5; N, 3·9%).

1-*Benzylamino*-2-n-*butylanthraquinone*.—The 1-nitro-derivative (1 g.) was refluxed with benzylamine (10 ml.) in presence of sodium acetate (1 g.), copper acetate (0·2 g.), and a trace of copper bronze for 5 hr., and the red solution was added to water. Chromatography from toluene gave a small pale yellow band and a main orange-red zone; the latter afforded deep brownish-red needles (0·63 g., 52·5%), m. p. 172—173° (from ethanol), of the 1-*benzylamino-derivative* (Found: C, 81·0; H, 6·15; N, 3·8. $C_{25}H_{23}O_2N$ requires C, 81·3; H, 6·3; N, 3·8%).

1-*Anilino*-2-n-*butylanthraquinone*.—The 1-nitro-derivative (1 g.) was heated under reflux

with dry aniline (15 ml.) and a little copper bronze for 12 hr., and the filtered mixture added to dilute aqueous hydrochloric acid. The resulting resin did not solidify or crystallise. Chromatography (chlorobenzene–alumina) gave a principal deep purple band which on extraction with ethanol (yield 0·57 g.) and crystallisation from acetic acid and then light petroleum (b. p. 60—80°) yielded bordeaux prisms, m. p. 105—106°, of the *anilino-derivative* (Found: C, 81·0; H, 6·1; N, 3·9. $C_{24}H_{21}O_2N$ requires C, 81·1; H, 6·0; N, 3·9%). Cellulose acetate rayon, Nylon, and Terylene were dyed dull shades of pink, slightly bluer than those derived from 1-anilinoanthraquinone, but of somewhat weaker colouring power.

1-*Amino*-4-*bromo*-2-n-*butylanthraquinone*.—(*a*) Bromination of 1-amino-2-*n*-butylanthraquinone (2·8 g., 1 mol.) in dilute hydrochloric acid was incomplete.

(*b*) Bromine (2·9 g., 1·15 mols.) in dry nitrobenzene (8 ml.) was added during 30 min., with stirring, to 1-amino-2-*n*-butylanthraquinone (4·4 g., 1 mol.) and fused sodium acetate (1·5 g.) in dry nitrobenzene (40 ml.) at 8—10°. The mixture was kept at 95° for 90 min.; nitrobenzene was removed with steam, and the residue (5 g.; m. p. 141—143°) was fractionated from alcohol to give orange needles (3·3 g.) of the pure bromo-derivative, m. p. 151—152° (Found: C, 60·1; H, 4·4; N, 3·9; Br, 22·3. Calc. for $C_{18}H_{16}O_2NBr$: C, 60·4; H, 4·45; N, 3·9; Br, 22·3%); the mother-liquors gave a similar product (Found: Br, 18·2%) (lit.,[4] m. p. 148°).

4-*Bromo*-2-n-*butyl*-1-*methylaminoanthraquinone*.—The procedure of method (*b*) above gave red prismatic needles, m. p. 81—82° (from ethanol), of 4-*bromo*-2-n-*butyl*-1-*methylaminoanthraquinone* (2 g., 70·2%) (Found: C, 61·2; H, 4·7; N, 3·8; Br, 21·7. $C_{19}H_{18}O_2NBr$ requires C, 61·3; H, 4·9; N, 3·8; Br, 21·5%).

2-n-*Butyl*-1 : 4-*bismethylaminoanthraquinone*.—4-Bromo-2-*n*-butyl-1-methylaminoanthraquinone (1·5 g.), 33% alcoholic methylamine (25 ml.), sodium acetate (1·5 g.), and copper acetate (0·2 g.) in a sealed tube at 120—125° for 2 hr. gave a solid (1·1 g.), chromatographed in toluene on alumina to yield a readily eluted bluish-red zone and a main bright blue zone, strongly adsorbed; the latter afforded deep violet needles with a metallic lustre, m. p. 178—179° (from ethanol) (0·57 g., 44%), of the *bismethylamino-derivative* (Found: C, 74·4; H, 6·6; N, 8·2. $C_{20}H_{22}O_2N_2$ requires C, 74·5; H, 6·8; N, 8·7%).

1 : 4-*Diamino*-2-n-*butylanthraquinone*.—1-Amino-4-bromo-2-*n*-butylanthraquinone (1·5 g.), aqueous ammonia (*d* 0·88; 24 ml.), sodium acetate (2 g.), copper acetate (0·2 g.), and alcohol (12 ml.) at 120—125° for 2 hr. gave a solid, and thence by chromatography in toluene, a main intense reddish-violet band; the *diamine* crystallised from ethanol in deep violet needles, m. p. 211—212° (0·8 g., 65%) (Found: C, 73·2; H, 6·0; N, 9·3. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·2; N, 9·5%). On cellulose acetate rayon, the reddish-violet shade was brighter and bluer than that derived from 1 : 4-diaminoanthraquinone; Nylon was dyed a bluish-violet shade, and Terylene a reddish-violet, similar to the dyeings from 1 : 4-diaminoanthraquinone.

Refluxing the diamine with acetic anhydride gave the *diacetamido-compound* which crystallised from benzene–light petroleum (b. p. 60—80°) in yellow needles, m. p. 233—234° (Found: C, 70·1; N, 5·7; N, 7·7. $C_{22}H_{22}O_4N_2$ requires C, 69·8; H, 5·9; N, 7·4%). The *dibenzamido-compound*, prepared by use of benzoyl chloride in nitrobenzene at 140°, crystallised from acetic acid in golden-orange needles, m. p. 251—252° (Found: C, 76·2; H, 5·2; N, 5·5. $C_{32}H_{26}O_4N_2$ requires C, 76·45; H, 5·2; N, 5·6%); chromatography in chlorobenzene showed it to be homogeneous.

Dinitration of 2-n-*Butylanthraquinone*.—Potassium nitrate (6·67 g., 2·2 mols.) was added to 2-*n*-butylanthraquinone (7·93 g., 1 mol.) in sulphuric acid (100 ml.) at <40° during 20 min., and the mixture kept at room temperature for 8 hr. The solid was collected in a sintered-glass funnel (acid liquor *A*) and extracted with boiling alcohol to give the insoluble 1 : 5-dinitro-compound (3·5 g.), pale yellow needles, m. p. 264—265° (from acetic acid) (Found: C, 60·9; H, 3·8; N, 7·8. Calc. for $C_{18}H_{14}O_6N_2$: C, 61·0; H, 4·0; N, 7·9%); the alcohol-soluble portion was chromatographed in toluene to yield (eluted) orange-yellow needles, m. p. 148°, of 2-*n*-butyl-1-nitroanthraquinone, and a yellow band (light-sensitive) which gave brownish-orange needles (0·5 g.), m. p. 176—177° (from ethanol), of pure 1 : 8-dinitro-derivative (Found: C, 60·8; H, 3·9; N, 7·9%); the product, m. p. 158° (ref. 4, p. 1630), was impure. The acid liquors *A* were added to water, and the solid (3·5 g.) extracted with boiling alcohol to yield insoluble 1 : 5-dinitro-derivative, m. p. 264°, and from the soluble portion a solid (*B*; 2·2 g.) which was purified by chromatography in toluene to yield (eluted) a little 1-nitro-derivative, m. p. 148° (Found: N, 4·35%), brownish-orange needles (0·4 g.), m. p. 176—177°, of the 1 : 8-dinitro-derivative, and unidentified products. The solid *B* (1 g.) was reduced by aqueous-alcoholic sodium sulphide

to give a solid (0·94 g.), whence chromatography in toluene yielded a little 1-amino-2-*n*-butylanthraquinone, m. p. and mixed m. p. 175—176°, which was eluted, and two bands which afforded the 1 : 8-diamine, m. p. and mixed m. p. 166°, and, more strongly adsorbed, orange-brown prisms (0·2 g.), m. p. 169—170° (from ethanol); the last product was rechromatographed, to give reddish-orange needles of a *substance*, m. p. 193—194° (Found: C, 73·4; H, 6·1; N, 9·3. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·2; N, 9·5%), and a lower band which afforded yellowish-orange needles of a substance, m. p. 240—245° (Found: N, 9·5%); these were not orientated, but were possibly the 1 : 6- and 1 : 7-diamino-derivative.

1 : 5- *and* 1 : 8-*Diamino*-2-n-*butylanthraquinone*.—Reduction of the pure 1 : 5-dinitro-compound (1 g.) with aqueous-alcoholic sodium sulphide gave yellowish-orange needles (0·73 g., 88·5%), m. p. 160°, of the 1 : 5-diamine (Found: C, 73·5; H, 6·1; N, 9·4. Calc. for $C_{18}H_{18}O_2N_2$: C, 73·5; H, 6·2; N, 9·5%). 1 : 5-*Diacetamido*-, orange needles (from ethanol), m. p. 239—240° (Found: C, 69·5; H, 5·9; N, 7·3. $C_{22}H_{22}O_4N_2$ requires C, 69·8; H, 5·9; N, 7·4%), and 1 : 5-*dibenzamido*-2-n-*butylanthraquinone*, yellow needles (from ethanol), m. p. 237—238° (alcohol) (Found: C, 76·6; H, 5·1; N, 5·8. $C_{32}H_{26}O_4N_2$ requires C, 76·45; H, 5·2; N, 5·6%), were prepared from this.

2-*n*-Butyl-1 : 8-dinitroanthraquinone (1 g.) similarly gave the 1 : 8-diamine (0·76 g., 92%), which crystallised from ethanol in brownish-red needles, m. p. 166° (Found: C, 73·4; H, 6·1; N, 9·7%); chromatography confirmed its homogeneity; but a sample, m. p. 140° (cf. ref. 4), was impure, probably containing 1-amino-derivative from a nitro-derivative which had not been removed by chromatography. 1 : 8-*Diacetamido*-, pale yellow needles, m. p. 240—241° (from ethanol) (admixture with the 1 : 5-isomer gave m. p. 210—212°) (Found: C, 69·5; H, 6·1; N, 7·4%), and the 1 : 8-*diacetamido*-2-n-*butylanthraquinone*, bright yellow needles, m. p. 242—243° (from ethanol) (Found: C, 76·5; H, 5·2; N, 5·6%), were shown to be homogeneous by chromatography and further crystallisation.

2-n-*Butyl*-1 : 5-*bismethylaminoanthraquinone*.—The 1 : 5-dinitro-compound (0·9 g.), 33% alcoholic methylamine (24 ml.), and sodium acetate (0·8 g.) in a sealed tube at 135—140° for 8 hr. gave a bluish-red solid (0·88 g.); chromatography in chlorobenzene separated a main deep reddish-purple band and thence reddish-brown needles with an intense bronze lustre (0·38 g.), m. p. 142—143° (from ethanol) (Found: C, 74·4; H, 6·7; N, 8·55. $C_{20}H_{22}O_3N_2$ requires C, 74·5; H, 6·8; N, 8·7%).

2-n-*Butyl*-1 : 8-*bismethylaminoanthraquinone*.—Prepared as above, this *base* crystallised from ethanol in reddish-brown needles with a bronze lustre, m. p. 104—105° (Found: C, 74·3; H, 6·8; N, 8·5%).

2-n-*Butyl*-1 : 5-*di*-(2-*hydroxyethylamino*)*anthraquinone*.—The 1 : 5-dinitro-compound (0·9 g.), freshly distilled 2-hydroxyethylamine (10 ml.), ethanol (5 ml.), and sodium acetate (0·8 g.), as above, gave after chromatography in *o*-dichlorobenzene two main zones, which yielded reddish-violet needles with a bronze lustre (0·28 g.), m. p. 171—172° (from ethanol) (Found: C, 70·7; H, 6·5; N, 8·2. $C_{20}H_{22}O_3N_2$ requires C, 71·0; H, 6·55; N, 8·3%), of 1(or 5)-*amino*-2-n-*butyl*-5(or 1)-2′-*hydroxyethylaminoanthraquinone*, and (more strongly adsorbed) magenta needles (0·24 g.), m. p. 148—149° (from ethanol) (Found: C, 69·1; H, 6·9; N, 7·15. $C_{22}H_{26}O_4N_2$ requires C, 69·1; H, 6·85; N, 7·3%), of 2-n-*butyl*-1 : 5-*di*-(2-*hydroxyethylamino*)*anthraquinone*.

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