331. *Anthraquinone Series. Part II. Nitro- and Amino-2-tert.-butyl- and -n-butyl-anthraquinones, and Derived Blue Acid Dyes.*

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A comparison of the derivatives of 2-*tert.*- (I) and 2-*n*-butylanthraquinone (II) shows the steric influence of the *tert.*-butyl group. Compound (I) could not be halogenated, and its *mononitro*-derivative is prepared with difficulty, whereas *chloro*-, *bromo*-, and *nitro*-derivatives of (II) are prepared readily. Unlike the tert.-*butyl* analogue, 1-*amino*-2-n-*butylanthraquinone* is readily acetylated; 1 : 5-*diamino*-2-tert.-*butylanthraquinone* affords a *monoacetyl* derivative only, whilst 1 : 5-*diamino*-2-n-*butylanthraquinone* gives a *diacetyl* derivative. Blue acid dyes for wool are obtained by converting 4-*bromo*-1-*amino*-2-tert.- and -2-n-*butylanthraquinone* into the respective 4-p-*toluidino*-derivatives, and sulphonating.

2-*tert.*-Butyl- (I) and 2-*n*-butyl-anthraquinone (II) were prepared in 75% and 72% yield, respectively, by direct cyclisation of the corresponding 2-(4′-butylbenzoyl)benzoic acid with 20% fuming sulphuric acid at 95° and 100°, respectively (Peters and Rowe, *J.*, 1945, 181). No derivative of (I) is recorded in the literature, and only the mono-nitro- and -amino-derivatives of (II) have been described (Harris, Marriott, and Smith, *J.*, 1936, 1838). The preparation, properties, and orientation of derivatives of (I) and (II) are now investigated, with special reference to the differing effects of the *tert.*- and *n*-butyl groups.

Nitration of 2-*tert.*-butylanthraquinone with nitric acid (*d* 1·42 or 1·5), alone or with acetic acid or anhydride, or sulphuric acid, or with diacetylorthonitric acid (Pictet and Genequand, *Ber.*, 1902, **35**, 2526), at various temperatures, yielded resinous products, but the use of potassium nitrate (1·1 mols.) in concentrated sulphuric acid at room temperature gave 46·2% of 1-*nitro*-2-tert.-*butylanthraquinone* (III). Repeated crystallisation from acetic acid was necessary in order to obtain a pure sample, as resin formation during nitration could not be completely avoided. Reduction of (III) by boiling aqueous–alcoholic sodium sulphide yielded 1-*amino*-2-tert.-*butylanthraquinone* (IV). The position accorded to the amino-group is supported by the formation of (IV) from (III) by aqueous ammonia (*d* 0·88) at 130° in a sealed tube, and by the fact that the *tert.*-butyl group inhibits formation of a crystalline acetyl or benzoyl derivative from (IV); diazotisation is accompanied by tar formation, but an *azo*-β-*naphthol* derivative was prepared. Further evidence that the amino-group is in the 1-position is afforded by bromination to the red 4-*bromo*-1-*amino*-2-tert.-*butylanthraquinone* (V) and its conversion into the deep blue 4-p-*toluidino*-analogue (VI), which on sulphonation yielded a blue acid wool dye. The amine (IV) condensed with 1-chloroanthraquinone in presence of sodium acetate and cuprous chloride to give a good yield of 2-tert.-*butyl-di*-1 : 1′-*anthraquinonylimide* (VII).

Dinitration of 2-*tert.*-butylanthraquinone gave 66·5% of 1 : 5-*dinitro*- (VIII) and 8·7% of 1 : 8-*dinitro*-2-tert.-*butylanthraquinone*, some (VIII) also being formed during mononitration of (I). Aqueous–alcoholic sodium sulphide reduction of the respective dinitro-compound afforded 1 : 5- (IX) and 1 : 8-*diamino*-2-tert.-*butylanthraquinone*. Orientation is based partly on analogy with the dinitration of anthraquinone and 2-methylanthraquinone. The steric effect of the *tert.*-butyl group in the diamine (IX) allowed the formation of a *monoacetyl* derivative only, whereas 1 : 5-diamino-2-*n*-butylanthraquinone readily gave a diacetyl derivative (see below).

1 : 5-*Di*-α-*anthraquinonylimino*-2-tert.-*butylanthraquinone* was formed in 78% yield from the diamine (IX), and a stabilised diazo-salt prepared from (IX) showed very similar properties to the analogue derived from 1 : 5-diaminoanthraquinone, both being only slightly decomposed after 3 hours at 95°. Moreover, bromination of the diamine (IX) gave a *tribromo*-derivative, which on refluxing with *p*-toluidine in presence of sodium acetate afforded probably 6-*bromo*-1 : 5-*diamino*-4 : 8-*di*-p-*toluidino*-2-tert.-*butylanthraquinone*; subsequent disulphonation gave a bluish-green dye for wool, with similar properties to that prepared by analogous means from 1 : 5-diaminoanthraquinone.

1-Nitro-2-*n*-butylanthraquinone, prepared in 70·6% yield from 2-*n*-butylanthraquinone, was readily reduced to the corresponding amine, which afforded an *acetyl* derivative (cf. the *tert* -butyl analogue) and an *azo*-β-*naphthol* derivative, and condensed with 1-chloroanthraquinone to give the corresponding *anthrimide*. The red 4-*bromo*-1-*amino*-2-n-*butylanthraquinone* was converted into the blue p-*toluidino*-analogue, and thence into the sulphonic acid, which dyes wool a deep blue shade, brighter than that given by the *tert.*-butyl analogue.

Dinitration of 2-*n*-butylanthraquinone yielded 61·5% of 1 : 5-dinitro- and 21% of 1 : 8-*dinitro*-2-n-*butylanthraquinone*, both being readily reduced to the corresponding 1 : 5- and 1 : 8-*diamines*, which afford *diacetyl* derivatives.

Under a variety of conditions, chlorination or bromination of 2-*tert.* butylanthraquinone was not achieved, whereas the 2-*n*-butyl isomeride gave 1-*chloro-* and -*bromo*-2-n-*butylanthraquinone* and a *dibromo*-derivative.

In general, derivatives of 2-*tert.*- and -*n*-butylanthraquinone are more soluble in organic solvents, and have a lower m. p., than the corresponding anthraquinone derivatives.

Experimental.

1-*Nitro*-2-tert.-*butylanthraquinone* (III).—Powdered potassium nitrate (12·2 g.; 1·2 mols.) was added during 15 minutes to a vigorously stirred solution of 2-*tert*,-butylanthraquinone (26·4 g.; 1 mol. in concentrated sulphuric acid (200 c.c.) at room temperature. After 6 hours' stirring, the mixture was left overnight and a small amount of insoluble dinitro-compound collected. Addition of the filtrate to ice–water gave a pale yellow solid, m. p. 115—120° (decomp., forming an opaque mass, which clarified at 160°); boiling with aqueous sodium hydrogen sulphite did not effect further purification, which was best carried out by repeated crystallisation from acetic acid, giving pale yellow needles, of constant m. p. 206—207°, of the *mononitro*-compound (III) (14·3 g.; 46·2%) (Found: C, 69·3; H, 4·9; N, 4·6. $C_{18}H_{15}O_4N$ requires C, 69·9; H, 4·85; N, 4·5%). No further pure nitro-derivative was isolable from the acetic acid mother liquors.

The insoluble *dinitro*-derivative crystallised from much acetic acid in almost colourless needles, m. p. 315° (2·2 g.; 6·2%) (Found: C, 60·5; H, 4·0; N, 7·6. $C_{18}H_{14}O_6N_2$ requires C, 61·0; H, 4·0; N, 7·9%) (see below).

1-*Amino*-2-tert.-*butylanthraquinone* (IV).—(*a*) Pure 1-nitro-2-*tert.*-butylanthraquinone (3 g.) was refluxed with sodium sulphide crystals (15 g.) in 50% aqueous alcohol (70 c.c.) for 40 minutes. On careful addition of water, the *amine* separated as a red solid; it crystallised from 90% alcohol in scarlet prismatic needles, m. p. 161° (2·3 g.; 85·2%) (Found: C, 77·5; H, 6·0; N, 5·1. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1; H, 5·0%). The amine gives a colourless sulphate with concentrated sulphuric acid, but it is a weak base, dilution quickly hydrolysing the salt. It is diazotisable, but attempted acetylation or benzoylation in presence of pyridine or nitrobenzene at various temperatures afforded tarry products which could not be crystallised. The crude nitration product (5·9 g.), m. p. 115—120° (decomp.), was reduced as above to yield dark brownish-red nodules, m. p. 70° (4·5 g.; 84·5%), which were chromatographed using alumina and benzene; the only pure product isolated was the above amine, m. p. and mixed m. p. 160—161°.

(*b*) 1-Nitro-2-*tert.*-butylanthraquinone (1 g.), m. p. 206—207°, was heated with aqueous ammonia (*d* 0·88; 20 c.c.) at 130° for 6 hours in a sealed tube. The brownish-red mass crystallised from 90% alcohol in red prismatic needless, m. p. 161° (0·4 g.), not depressed on admixture with the amine obtained by method (*a*).

Derivatives of the Amine (IV).—Diazotisation in cold concentrated sulphuric acid was not neat, there being some tar formation, but subsequent coupling with alkaline β-naphthol gave 35% of the *azo-β-naphthol* derivative, which crystallised from acetic acid in reddish-brown prismatic needles, m. p. 222° (Found: N, 6·1. $C_{28}H_{22}O_3N_2$ requires N, 6·5%), soluble in cold concentrated sulphuric acid to give a blue solution.

The amine (1 g.; 1 mol.) was refluxed with 1-chloroanthraquinone (0·95 g.; 1·1 mols.), anhydrous sodium acetate (1·2 g.), cuprous chloride (0·2 g.), and nitrobenzene (16 c.c.) for 6 hours. Dilution with alcohol (40 c.c.) gave a precipitate of 2-tert.-*butyl-di*-1 : 1′-*anthraquinonylimide* (1·5 g.; 86·2%), which crystallised from benzene in brownish-red prismatic needles, m. p. >360° (Found: N, 2·6. $C_{32}H_{23}O_4N$ requires N, 2·9%).

4-*Bromo*-1-*amino*-2-tert.-*butylanthraquinone* (V).—1-Amino-2-*tert.*-butylanthraquinone (2 g.) was dissolved in nitrobenzene (15 c.c.), and fused sodium acetate (0·7 g.) added. Bromine (1·8 g.; 1·5 mols.) in nitrobenzene (6 c.c.) was added at 8°, and, after 30 minutes' stirring at room temperature, the temperature was raised gradually to 95° and kept there for 1 hour. A little solid (0·2 g.) separated, and was collected, washed with aqueous sodium carbonate and then alcohol, and crystallised from nitrobenzene to give glistening, scarlet prismatic needles, decomp. at *ca.* 320° (Found: Br, 47·0. $C_{18}H_{14}O_2NBr_3$ requires Br, 46·5%), of a *tribromo*-derivative.

After removal of the nitrobenzene with steam, the main reaction product of 4-*bromo*-1-*amino*-2-tert.-*butylanthraquinone* crystallised from alcohol in red prismatic needles, m. p. 158° (2 g.; 78·2%) (Found: C, 60·0; H, 4·2; N, 4·2; Br, 22·6. $C_{18}H_{16}O_2NBr$ requires C, 60·3; H, 4·5; N, 3·9; Br, 22·3%).

1-*Amino*-4-p-*toluidino*-2-tert.-*butylanthraquinone* (VI).—The above 4-bromo-compound (1 g.) was heated with *p*-toluidine (3 g.), anhydrous sodium acetate (1 g.), and copper acetate (0·1 g.) at 95° for 16 hours. Alcohol (20 c.c.) was added; the separated 4-p-*toluidino*-derivative (VI) crystallised from pyridine in deep blue needles, m. p. 135° (0·7 g.; 65·1%) (Found: C, 77·6; H, 5·6; N, 7·9. $C_{25}H_{24}O_2N_2$ requires C, 78·1; H, 6·2; N, 7·3%). Confirmation that the compound had the constitution assigned was afforded by sulphonation with 5% fuming sulphuric acid at 30° for 6 hours; on salting out the product from aqueous solution with sodium sulphate, a sulphonic acid was obtained which dyes wool from an acetic acid and sodium sulphate bath a blue shade of similar light fastness to that shown by the 2-methyl analogue, *viz.*, Solway Blue RNS.

Dinitration of 2-tert.-*Butylanthraquinone* : 1 : 5- *and* 1 : 8-*Dinitro-compounds.*—Powdered potassium nitrate (10 g.; 2·2 mols.) was added during 15 minutes to a solution of 2-*tert.*-butylanthraquinone (12 g.) in concentrated sulphuric acid (140 c.c.) at 40°; after 6 hours' stirring at this temperature, the precipitate was collected; the 1 : 5-*dinitro*-2-tert.-*butylanthraquinone* crystallised from acetic acid in almost colourless needles, m. p. 315° (10·7 g.; 66·5%), identical with the dinitro-compound formed during mononitration (above). The 1 : 5-dinitro-derivative is very sparingly soluble in alcohol.

The sulphuric acid filtrate was poured on ice, and the resulting solid crystallised several times from alcohol to yield pale yellow needles, m. p. 170° (1·6 g.; 8·7%), of the 1 : 8-*dinitro*-isomeride (Found: C, 60·1; H, 3·9; N, 7·7. $C_{18}H_{14}O_6N_2$ requires C, 61·0; H, 4·0; N, 7·9%).

1 : 5- *and* 1 : 8-*Diamino*-2-tert.-*butylanthraquinone.*—The respective dinitro-compounds (2 g.) were

reduced by refluxing them with sodium sulphide crystals (20 g.) in 50% aqueous alcohol (100 c.c.) for 1 hour.

1 : 5-*Diamino*-2-tert.-*butylanthraquinone* crystallised from alcohol in glistening red leaflets, m. p. 158° (1·7 g.; 91%) (Found : C, 72·9; H, 5·95; N, 9·5. $C_{18}H_{18}O_2N_2$ requires C, 73·4; H, 6·1; N, 9·5%). It is strongly basic, and dissolves in hydrochloric acid to give a pale yellow solution, and is easily diazotisable to yield stable diazo-solutions.

The 1 : 5-diamine (0·5 g.) was dissolved in concentrated hydrochloric acid (3 c.c.) and sodium nitrite (0·75 g.) added slowly at 10°, with stirring. After 30 minutes, anhydrous sodium sulphate (2·5 g.) was added and the pale brown diazonium salt was collected and dried (2·3 g., 26·5% strength; 92%). After 3 hours' heating at 35°, 55°, 75°, and 95°, the strengths as determined by titration with alkaline β-naphthol were 26·5, 26, 25, and 24·4%, respectively, indicating very good stability to heat; in this respect, the diamine resembles 1 : 5-diaminoanthraquinone.

A stabilised diazo-compound was also readily formed as the zinc chloride double salt.

The *bisazo-β-naphthol* derivative crystallised from benzene in bordeaux needles, with a green reflex, m. p. 298° (Found : N, 9·5. $C_{38}H_{28}O_4N_4$ requires N, 9·3%), which dissolve in cold concentrated sulphuric acid with a violet colour.

On refluxing with acetic anhydride for 4 hours, the 1 : 5-diamine gave the *monoacetyl* derivative, which separated in brick-red glistening prismatic needles; crystallisation from alcohol gave deep claret prisms, m. p. 244° (Found : C, 70·1; H, 6·4; N, 8·2; Ac, 13·7. $C_{22}H_{22}O_4N_2$ requires C, 69·8; H, 5·8; N, 7·4; Ac, 22·8. $C_{20}H_{20}O_3N_2$ requires C, 71·4; H, 6·0; N, 8·3; Ac, 12·9%).

1 : 5-Diamino-2-*tert.*-butylanthraquinone (0·4 g.) was refluxed with 1-chloroanthraquinone (0·8 g.), anhydrous sodium acetate (0·3 g.), cuprous chloride (0·1 g.), and nitrobenzene (6 c.c.) for 6 hours; the precipitate which separated on cooling crystallised from benzene in bordeaux plates, m. p. >360° (0·7 g.; 78%), of 1 : 5-*di-α-anthraquinonylimino*-2-tert.-*butylanthraquinone* (Found : N, 4·2. $C_{46}H_{30}O_6N_2$ requires N, 3·9%), soluble in cold concentrated sulphuric acid to give a deep blue solution.

1 : 8-*Diamino*-2-tert.-*butylanthraquinone* crystallised from alcohol in reddish-brown needles, m. p. 143° (1·4 g.; 75·3%) (Found : C, 72·8; H, 5·8; N, 9·3. $C_{18}H_{18}O_2N_2$ requires C, 73·4; H, 6·1; N, 9·5%), difficultly soluble in hydrochloric acid and not readily diazotisable.

(?) 4 : 6 : 8-*Tribromo*-1 : 5-*diamino*-2-tert.-*butylanthraquinone, and its Conversion into a Bluish-green Wool Dye.*—The 1 : 5-diamine (1 g.) was treated in acetic acid solution (100 c.c.) with excess of bromine (5 g.) and the mixture was refluxed for 3 hours; the deep red product which separated was washed with warm aqueous sodium carbonate; it crystallised from nitrobenzene in claret needles, m. p. >360° (1·3 g.; 71·4%) (Found : Br, 45·6. $C_{18}H_{15}O_2N_2Br_3$ requires Br, 45·2%), of the *tribromo*-compound. On refluxing 1 g. with *p*-toluidine (10 g.) and sodium acetate (2 g.) for 6 hours, the colour changed through violet to bluish-green; after cooling, the resulting precipitate was collected, washed well with dilute hydrochloric acid, and then aqueous sodium carbonate and water; it crystallised from pyridine in deep bluish-green needles, m. p. 260—261° (0·7 g.; 63·6%) (Found : N, 9·5; Br, 14·2. $C_{32}H_{31}O_2N_4Br$ requires N, 9·7; Br, 13·7%).

(?) 6-*Bromo*-1 : 5-*diamino*-4 : 8-*di*-p-*toluidino*-2-tert.-*butylanthraquinone* was sulphonated with 100% sulphuric acid at 30° for 20 minutes, and the disulphonic acid purified by careful salting out from aqueous solution with sodium sulphate. It dyes wool a bright greenish-blue shade, similar to that given by the analogous 2-methyl derivative.

Attempted Halogenation of 2-tert.-*Butylanthraquinone.*—Direct chlorination in various solvents, or the use of sulphuryl chloride in nitrobenzene (with a little iodine) at 95° for 6 hours, gave unchanged material; sulphuryl chloride and nitrobenzene in a sealed tube at 160° for 5 hours afforded a resin.

2-*tert.*-Butylanthraquinone was unchanged with bromine in nitrobenzene in presence of sodium acetate at 95—160° for 4 hours, and bromination in 20% fuming sulphuric acid at 100—130° gave a resin.

1-*Nitro*-2-n-*butylanthraquinone.*—Potassium nitrate (6·3 g.; 1·2 mols.) was added to 2-*n*-butylanthraquinone (13·2 g.; 1 mol.) in concentrated sulphuric acid (100 c.c.) during 20 minutes, at room temperature, and the mixture was stirred at 45° for 6 hours and left overnight at room temperature. The solid which had separated crystallised from acetic acid in pale yellow needles, m. p. 260°, of 1 : 5-dinitro-2-*n*-butylanthraquinone (2·5 g.; 14·1%) (see below). Dilution of the sulphuric acid filtrate gave 1-nitro-2-*n*-butylanthraquinone, which crystallised from acetic acid in pale yellow needles, m. p. 150° (10·9 g.; 70·6%) (Found : C, 70·0; H, 4·7; N, 4·3. Calc. for $C_{18}H_{15}O_4N$: C, 69·9; H, 4·85; N, 4·5%).

1-*Amino*-2-n-*butylanthraquinone.* The above mononitro-compound (5 g.) was refluxed with sodium sulphide crystals (30 g.) in 50% aqueous alcohol (120 c.c.) for 1 hour, and, on addition of water, the amine separated; it crystallised from aqueous alcohol in long, red prismatic needles, m. p. 172° (4·2 g.; 91·3%) (Found : C, 77·1; H, 6·0; N, 5·0. Calc. for $C_{18}H_{17}O_2N$: C, 77·4; H, 6·1; N, 5·0%). Its *acetyl* derivative separated from acetic anhydride (boil for 3 hours), and crystallised from 50% aqueous alcohol in yellow needles, m. p. 140° (Found : N, 4·3. $C_{20}H_{19}O_3N$ requires N, 4·4%). The amine was diazotised in sulphuric acid, and afforded an *azo-β-naphthol* derivative, which crystallised from acetic acid in brownish-red plates, m. p. 243° (Found : N, 6·0. $C_{28}H_{22}O_3N_2$ requires N, 6·5%).

2-n-*Butyl-di*-1 : 1′-*anthraquinonylimide*, prepared by heating with 1-chloroanthraquinone, as above, crystallised from benzene in brownish-red needles, m. p. >360° (Found : N, 2·7. $C_{32}H_{23}O_4N$ requires N, 2·9%).

4-*Bromo*-1-*amino*-2-n-*butylanthraquinone.*—Prepared in similar manner to that used for the *tert.*-butyl analogue, the 4-*bromo*-derivative formed red prismatic needles (alcohol), m. p. 148° (78%) (Found : N, 4·5; Br, 22·3. $C_{18}H_{16}O_2NBr$ requires N, 4·5; Br, 22·3).

1-*Amino*-4-p-*toluidino*-2-n-*butylanthraquinone.*—This *compound* crystallised from pyridine in blue needles, m. p. 145° (72%) (Found : C, 78·4; H, 5·5; N, 7·7. $C_{25}H_{24}O_2N_2$ requires C, 78·1; H, 6·2; N, 7·3%), which on sulphonation at 30°, as above, yielded a sulphonic acid which dyes wool from an acetic acid and Glauber's salt bath a deep blue shade brighter than that afforded by the *tert.*-butyl analogue.

Dinitration of 2-n-*Butylanthraquinone* : 1 : 5- *and* 1 : 8-*Dinitro-compounds.*—Potassium nitrate (7 g.; 2·2 mols.) was added during 20 minutes to a stirred solution of 2-*n*-butylanthraquinone (8 g.;

1 mol.) in concentrated sulphuric acid (100 c.c.) at 40°. After 6 hours stirring at this temperature, the crystals were collected; recrystallisation from acetic acid gave yellow needles, m. p. 260° (6·4 g.; 61·5%) (Found : C, 61·4; H, 4·0; N, 7·7. $C_{18}H_{14}O_6N_2$ requires C, 61·0; H, 4·0; N, 7·9%), of 1 : 5-*dinitro*-2-n-*butylanthraquinone*.

The sulphuric acid filtrate was poured on ice, and the yellow precipitate crystallised several times from alcohol, to yield yellow needles, m. p. 158°, of 1 : 8-*dinitro*-2-n-*butylanthraquinone* (2·2 g.; 21·1%) (Found : C, 61·5; H, 3·9; N, 7·8%).

1 : 5- *and* 1 : 8-*Diamino*-2-n-*butylanthraquinone*.—The 1 : 5-diamine crystallised from alcohol in large orange-red needles, m. p. 160° (90%) (Found : C, 72·9; H, 6·3; N, 9·2. $C_{18}H_{18}O_2N_2$ requires C, 73·4; H, 6·1; N, 9·5%).

The 1 : 5-diamine readily formed a stable diazonium salt (cf. the *tert.*-butyl analogue), which was very stable to heat; thus, a salt of 19% strength on being heated at 75° or 95° for 3 hours was reduced in strength to 18 or 17·6%, respectively. A stable *iso*diazoate was also formed readily.

The *bisazo-β-naphthol* derivative crystallised from benzene in brownish-red needles, m. p. 298—300° (Found : N, 8·7. $C_{38}H_{28}O_4N_4$ requires N, 9·2%).

With boiling acetic anhydride for 3 hours, the 1 : 5-diamine gave a *diacetyl* derivative, which crystallised from alcohol in yellow needles, m. p. 182° (Found : N, 8·0; Ac, 24·4. $C_{22}H_{22}O_4N_2$ requires N, 7·4; Ac, 22·8%).

The *dianthrimide*, prepared by refluxing the 1 : 5-diamine with 1-chloroanthraquinone as above, crystallised from benzene in deep claret needles, m. p. >360° (Found : N, 4·3. $C_{46}H_{30}O_6N_2$ requires N, 3·9%), which dissolved in cold concentrated sulphuric acid to give a deep blue solution.

1 : 8-*Diamino*-2-n-*butylanthraquinone* crystallised from alcohol in reddish-brown needles, m. p. 140° (Found : N, 9·3. $C_{18}H_{18}O_2N_2$ requires N, 9·5%), and gave a *diacetyl* derivative, which crystallised from alcohol in yellowish-brown needles, m. p. 152° (Found : N, 7·9. $C_{22}H_{22}O_4N_2$ requires N, 7·4%).

1-*Chloro*-2-n-*butylanthraquinone*.—2-*n*-Butylanthraquinone (1·5 g.) was heated gradually with sulphuryl chloride (1 g.), iodine (0·2 g.), and nitrobenzene (8 c.c.), and finally heated under reflux on the water-bath for 5 hours. The nitrobenzene was removed with steam; the residue of *chloro*-compound crystallised from alcohol in cream needles, m. p. 74° (1·2 g.; 69%) (Found : Cl, 11·4. $C_{18}H_{15}O_2Cl$ requires Cl, 11·9%).

1-*Bromo*-2-n-*butylanthraquinone*.—Bromine (2·5 g.; 1·2 mols.) was added to a solution of 2-*n*-butylanthraquinone (3 g.; 1 mol.) in nitrobenzene (15 c.c.), in presence of anhydrous sodium acetate (1 g.) at 8°, and the temperature was raised gradually to 95° and kept there for 3 hours. The mixture was added to alcohol (40 c.c.) and left overnight; the precipitate crystallised from nitrobenzene in yellow needles, m. p. 149—150°, of a *dibromo*-derivative (0·5 g.; 10·4%) (Found : C, 51·6; H, 3·6; Br, 37·3. $C_{18}H_{14}O_2Br_2$ requires C, 51·2; H, 3·3; Br, 37·9%). After removal of the solvent from the alcohol–nitrobenzene filtrate by steam distillation, the resulting yellow solid crystallised from alcohol in yellow needles, m. p. 95°, of 1-*bromo*-2-n-*butylanthraquinone* (1·7 g.; 43·8%) (Found : C, 62·2; H, 4·2; Br, 24·2. $C_{18}H_{15}O_2Br$ requires C, 63·0; H, 4·4; Br, 23·3%). Analysis suggested that a little of the dibromo-compound was present.

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