221. *The Formation of* 1 : 2-7 : 8-*Diphthaloylcarbazole by Dehydrogenation of* 1 : 1′-*Dianthraquinonylamine.*

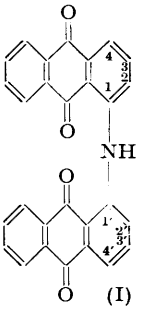
By William Bradley and Colin R. Thitchener.

Whilst the action of fused alkali hydroxides on 6 : 6′-di*meso*benzanthronylamine leads to hydrolysis and formation of 6-hydroxy*meso*benzanthrone, both 1 : 2′- and 2 : 2′-dianthraquinonylamine yield alizarin as the main product. In these instances hydroxylation precedes hydrolysis. 1 : 1′-Dianthraquinonylamine behaves otherwise. Hydroxylation and hydrolysis proceed only in minor degree, the main reaction being cyclisation to 1 : 2-7 : 8-diphthaloylcarbazole. The further action of alkali on the product yields 1 : 2-phthaloylcarbazole and an acid from which carbazole results on heating with soda-lime. The cyclisation reaction requires the presence of two anthraquinone nuclei. Its rate depends on the alkali employed. The mechanism of the reaction is considered to be analogous to the formation of di*meso*benzanthronyl from *meso*benzanthrone and of di-(1 : 9-pyrazoloanthron-2-yl) from 1 : 9-pyrazoloanthrone. The identity of the products obtained by heating 1 : 1′-dianthraquinonylamine with potassium hydroxide and with aluminium chloride is confirmed.

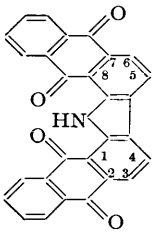
In earlier communications an account has been given of the self-coupling of *meso*benzanthrone, three isomeric benzo*meso*benzanthrones, pyridino*meso*benzanthrone and 1 : 9-pyrazoloanthrone by processes of dehydrogenation brought about by alkalis (Bradley and Jadhav, *J.*, 1948, 1622; Bradley and Sutcliffe, *J.*, 1952, 1247, 2118; Bradley and Geddes, *J.*, 1952, 1636). The present investigation is concerned with the analogous conversion of 1 : 1′-dianthraquinonylamine (I) into 1 : 2-7 : 8-diphthaloylcarbazole (II), in which, as in the examples given, two aromatic nuclei become united through carbon atoms situated *para* to carbonyl groups.

Early work (D.R.-P. 230,407, 240,080, 251,021; 262,788) indicated that alkali and aluminium chloride converted 1 : 1′-dianthraquinonylamine into indanthrone derivatives, but further investigation (D.R.-P. 267,522; 267,833) showed that the yellow product was, in both cases, more probably 1 : 2-7 : 8-diphthaloylcarbazole (II).

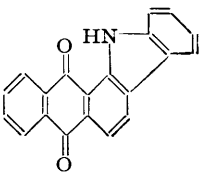
In the present work, (I) was first heated with aluminium chloride by the method given in B.I.O.S. Final Report, No. 1493, p. 53 (London, H.M.S.O.). The product, which had the properties recorded in the literature, was further characterised by its absorption spectrum in sulphuric acid (see Figure). For the potassium hydroxide fusion, it was



(I)

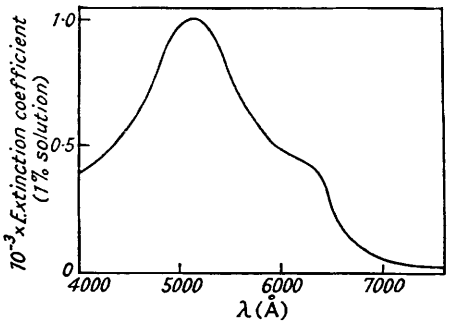


(II)



(III)

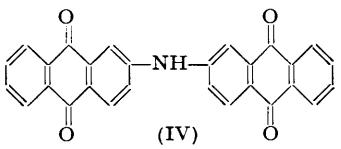
found that at 220° the main product was yellow-brown, as described in D.R.-P. 230,407, and that crystallisation followed by sublimation gave a bright yellow colouring matter having the same absorption spectrum in sulphuric acid as that obtained by use of aluminium



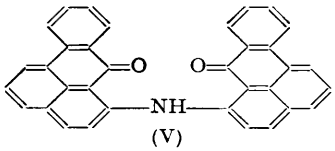
Absorption spectrum of a 0·001% *solution of* 1 : 2-7 : 8-*diphthaloylcarbazole in concentrated sulphuric acid.*

chloride. Other products of this reaction were 1 : 2-phthaloylcarbazole (III), anthraquinone, a trace of alizarin, and an acid which gave carbazole when heated with soda-lime.

The correctness of the constitution (II) assigned to the main product was confirmed by further heating of the purified material with potassium hydroxide at 220°; 1 : 2-phthaloylcarbazole (III) was formed, with an acid derived from carbazole. From this experiment it is probable that (III), when formed by the alkali fusion of (I), is derived by the decomposition of (II).



(IV)



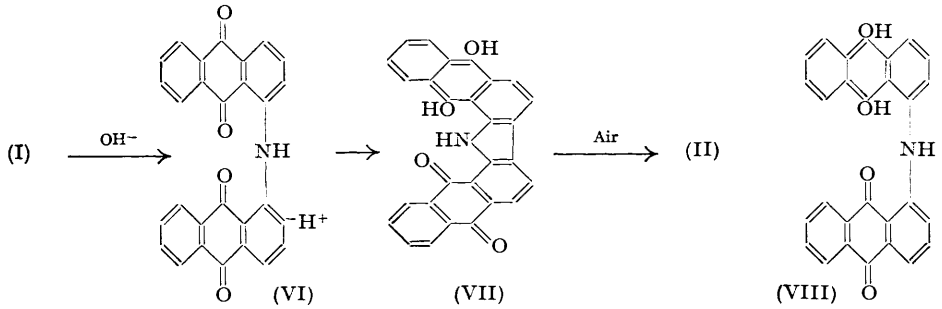
(V)

In yielding a carbazole derivative as the main product of alkali fusion (I) differs markedly from both 1 : 2′- and 2 : 2′-dianthraquinonylamine (IV) which under similar conditions yield alizarin and ammonia but no derivative of carbazole. It also differs from 6 : 6′-di*meso*benzanthronylamine (V) which, even with amyl-alcoholic potassium hydroxide, is readily hydrolysed to 6-amino- and 6-hydroxy-*meso*benzanthrone (Bradley, *J.*, 1948, 1175).

A further study of 2 : 2′-dianthraquinonylamine showed that indanthrone was absent from the product of alkali fusion, an indication that, unlike (V), the amine did not undergo initial hydrolysis to 2-hydroxy- and 2-amino-anthraquinone (for the conversion of 2-amino-anthraquinone into indanthrone see D.R.-P. 129,845 and Bradley and Leete, *J.*, 1951, 2129). It is probable that, like 2-anilinoanthraquinone (Bradley and Leete, *loc. cit.*),

2 : 2′-dianthraquinonylamine is first hydroxylated in the 1-position, and subsequently hydrolysed to give alizarin.

In the conversion of (I) into (II) the product is initially obtained in the form of an alkali-soluble reduction product from which (II) is precipitated on aeration. These changes are consistent with the following scheme (cf. Bradley and Geddes, *loc. cit.*).



It should be mentioned that the cyclisation of (I) to (II) is dependent on the presence of two quinone nuclei. Neither 1- nor 2-anilinoanthraquinone yields a carbazole derivative on fusion with alkali.

The formation of anthraquinone as a by-product of the reaction is of interest. It is possible that the intermediate (VII) reduces some of the starting material to (VIII), from which anthraquinone results by elimination of 1-aminoanthraquinone. Such a reaction would be analogous to the fission of 2-amino-1 : 2′-dianthraquinonylamine following reduction (Bradley and Leete, *J.*, 1951, 2160).

Cyclisation of (I) to (II) also occurs when sodium hydroxide replaces potassium hydroxide. At 220° the reaction proceeds much more slowly, but at 280° sodium hydroxide is as effective as potassium hydroxide at the lower temperature. Cæsium hydroxide, however, is as effective as potassium hydroxide. Thus the basic strength of the condensing agent is a factor in the cyclisation. The addition of a small proportion of phenol facilitates cyclisation by promoting adequate mixing, the composition of the product remaining substantially unaltered.

Attempts to prepare the *N*-methyl derivative of (I) were unsuccessful. It was hoped to employ it to establish whether the free –NH– group of (I) plays an essential part in the ring-closure : this appeared improbable since in the case of 1 : 9-pyrazoloanthrone sodium anilide causes the union of two nuclei whether the starting material is *N*-methylated or not (Bradley and Geddes, *loc. cit.*). The difficulty in methylating (I) is doubtless related to its stability as a molecule. It does not easily form a potassium derivative when methanolic potassium hydroxide is added to its solution in pyridine. 2 : 2′-Dianthraquinonylamine on the contrary readily forms a potassium salt, and *N*-methylation presents no difficulty (Bradley and Leete, *J.*, 1951, 2138).

The occurrence of hydroxylation with (IV) and of cyclisation with (I) provides a further illustration of the close connection between hydroxylation and self-coupling processes brought about by alkali hydroxides. Both reactions are theoretically possible with (I) and (IV) and it is probable that the result is determined by their relative rates in the two instances. A similar relation has been observed for 1- and 2-hydroxyanthraquinone. The first yields 1 : 1′-dihydroxy-2 : 2′-dianthraquinonyl (Scholl, Schwinger, and Dischendorfer, *Ber.*, 1919, **52**, 2254) whilst the second gives mainly alizarin (Liebermann, *Ber.*, 1871, **4**, 108; Baeyer and Caro, *ibid.*, 1874, **7**, 968). In the present work 1-aminoanthraquinone gave a product which could not be identified; it did not contain more than a trace of alizarin. 1-Anilinoanthraquinone gave alizarin but much of the product was recovered unchanged; both 2-amino- and 2-anilino-anthraquinone afford 1-hydroxy-derivatives (Bradley and Leete, *loc. cit.*). Hydroxylation in the 1-position is thus a common reaction with 2-derivatives of anthraquinone but an analogous reaction occurs less readily with the isomeric 1-substituted compounds. The difference in ease of substitution, which is determined by the difference in nuclear reactivity in the two series, may have its origin in

a difference of structure, the 1-derivatives (less reactive) approaching typical aromatic forms more closely. From this point of view it is the difficulty of hydroxylating (I) that allows coupling through the 2- and 2′-positions.

The cyclisation of (I) to (II) by means of aluminium chloride (B.I.O.S., *loc. cit.*) was studied in detail. Neither alizarin nor 1 : 2-phthaloylcarbazole was obtained at 140°; at 250° the product contained (II), but little or none of its reduced form (VII). 1 : 2-7 : 8-Diphthaloylcarbazole was readily isolated by subliming the crude product or by extracting it with methyl phthalate. There was no evidence of the presence of reduced forms capable of dehydrogenation by azobenzene, methylene-blue, or bromanil.

When aluminium chloride is used it is probable that the cyclisation follows the same course as with potassium hydroxide, except that the electron-seeking carbon atom at the 2′-position (see VI) results from valency changes following co-ordination of the oxygen atoms with the catalyst.

During the work a number of related matters were studied. Scholl, Schwinger, and Dischendorfer (*loc. cit.*) showed that 1-hydroxyanthraquinone, a possible hydrolysis product of (I), yields a reduced form of 1 : 1′-dihydroxy-2 : 2′-dianthraquinonyl on fusion with alkali. These reactions were confirmed, also conversion of the product into 1 : 2-7 : 8-diphthaloyldibenzofuran. None of these three compounds was found in the crude product obtained by heating (I) with potassium hydroxide, an indication that in this reaction, hydrolysis, if it occurs, is not an important step. It was also observed that sodium hydroxide was much less effective than potassium hydroxide in the self-condensation of 1-hydroxyanthraquinone.

In attempts to prepare *N*-methylated substitution products of (I), 2-nitro- and 4 : 4′-dinitro-1 : 1′-dianthraquinonylamine (D.R.-P. 254,186) were prepared. Both were stronger acids than (I) and readily gave characteristic colour reactions with methanolic potassium hydroxide in pyridine, but neither these nor (V) could be methylated with potassium carbonate and methyl toluene-*p*-sulphonate in trichlorobenzene. 1-Methylaminoanthraquinone did not condense with 1-chloro-2-nitroanthraquinone in the absence of a catalyst. With potassium acetate and cuprous chloride in nitrobenzene 1-methylaminoanthraquinone and 1-chloroanthraquinone afforded (I), demethylation having occurred (Bradley and Leete, *J.*, 1951, 2147).

Experimental

Action of Potassium Hydroxide on 2 : 2′-Dianthraquinonylamine.—(*a*) 2 : 2′-Dianthraquinonylamine (2·0 g.) was added at 180° to potassium hydroxide (20 g.) and water (2 c.c.). The temperature was raised to 220° during 30 minutes. A purple colour developed and ammonia was liberated. After 15 minutes longer the melt was added to water (200 c.c.), and the suspension was aerated for 24 hours. Filtration gave a purple solution from which a brown solid (1·8 g.) separated on the addition of acid. On sublimation it gave alizarin, 2 : 2′-dianthraquinonylamine, and a small amount of a black, non-volatile product. A similar result was obtained when the fusion was carried out in the presence of phenol (0·2 g.); in this case sublimation of a portion *in vacuo* gave alizarin (0·017 g.), 2 : 2′-dianthraquinonylamine (0·041 g.), and residue (0·012 g.).

(*b*) 2 : 2′-Dianthraquinonylamine (4 g.) was added to potassium hydroxide (50 g.) and water (5 c.c.) at 200°, and the temperature was raised slowly to 230—240° and maintained for 30 minutes. Ammonia was liberated and a violet melt resulted. This was added to water (500 c.c.), heated to boiling, and aerated for 12 hours, and the purple solution filtered from a blue residue. The filtrate afforded 2·7 g. of alizarin, and no other product could be detected by sublimation or chromatography from chlorobenzene on alumina. The blue residue (1·0 g.; m. p. 480—500°) gave a solution of the same colour in concentrated sulphuric acid. In pyridine it gave an orange solution, changed to bright green on the addition of methyl-alcoholic potassium hydroxide, and this remained stable on the further addition of a small volume of water or a considerable volume of alcohol. Much water caused the restoration of the original orange colour. Sublimed from a bath at 380—400°/0·5 mm. the blue product gave 2 : 2′-dianthraquinonylamine, a trace of alizarin, and a small non-volatile residue, only a small portion of which dissolved in warm alkaline dithionite solution. There was no evidence of the presence of indanthrone. The presence of alizarin and 2 : 2′-dianthraquinonylamine in the crude

product and the absence of indanthrone were confirmed by extraction with warm alkaline dithionite and chromatography of the resulting solution on cellulose.

Action of Potassium Hydroxide on 1 : 2′-*Dianthraquinonylamine.*—(*a*) 1 : 2′-Dianthraquinonylamine (1·0 g.) was added at 180° to potassium hydroxide (10 g.) and water (1 c.c.). The temperature was then raised to 220° during 30 minutes, and maintained for 20 minutes. The violet product was added to water (250 c.c.), and the resulting suspension was heated to boiling and aerated for 6 hours. It was acidified and the brown precipitate (1·0 g.) collected, washed, and dried. Sublimation of 0·082 g. at 140—150°/1 mm. for 3 hours gave alizarin (0·017 g.) and further sublimation at 360°/1 mm. gave unchanged 1 : 2′-dianthraquinonylamine (0·050 g.). There was a non-volatile residue (0·011 g.) which was insoluble in warm alkaline dithionite solution.

(*b*) The foregoing experiment was repeated with the addition of phenol (0·3 g.) to the alkali melt. After 45 minutes at 220° the products obtained when a portion was heated *in vacuo* were alizarin (0·045 g.), 1 : 2′-dianthraquinonylamine (0·019 g.), and a non-volatile residue, insoluble in alkaline dithionite solution (0·020 g.).

Action of Potassium Hydroxide on 1 : 1′-*Dianthraquinonylamine.*—(*a*) 1 : 1′-Dianthraquinonylamine (5 g.) was added to potassium hydroxide (50 g.) and water (5 c.c.) and heated as described in D.R.-P. 230,407. The brown melt was added to water (500 c.c.), heated to boiling, aerated for 12 hours, and then filtered; it afforded a brown solid (A) (4·4 g.) and a violet solution. The solution on acidification gave a gelatinous, brown precipitate (0·2 g.), and this on washing, drying, dissolving in chlorobenzene, and chromatography on alumina gave four bands. The most strongly absorbed was dark brown. It was followed by a bluish-red zone, and this on extraction with acetic acid gave orange-brown needles of alizarin, m. p. and mixed m. p. 284—286°. The solid (A) decomposed at >400°. Crystallisation from diethyl phthalate gave orange needles. Sublimation of (A) at 360—380°/0·2—0·4 mm. gave five zones. The most volatile product, pale yellow needles, crystallised from acetic acid as colourless needles, m. p. 282°, not depressed on admixture with anthraquinone, m. p. 283°, and having the properties thereof. The next zone was red and very small. The adsorbed colouring matter was insoluble in 5% potassium hydroxide, gave an orange solution in alkaline sodium dithionite, and dissolved in concentrated sulphuric acid with a yellow brown colour, and in pyridine forming a red solution which remained unaltered on the addition of methanolic potassium hydroxide. The third zone consisted of orange needles, m. p. 249—250°, not depressed on admixture with 1 : 2-phthaloylcarbazole, m. p. 251°. It gave a deep blue solution in concentrated sulphuric acid, changing to purple on warming. It dissolved in pyridine with a golden-yellow colour, changing to deep green on the addition of methanolic potassium hydroxide; the green colour was stable towards the addition of a small proportion of water, but further dilution regnerated the initial yellow colour. The fourth zone consisted of 1 : 1′-dianthraquinonylamine. The fifth band consisted of a dense mass of yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole, very sparingly soluble in pyridine. It gave a red solution in concentrated sulphuric acid the absorption spectrum of which was identical with that of the compound described in B.I.O.S. Final Report No. 1493, p. 53 (Figure). It decomposed without melting at >400°. The residue from the sublimation of (A) was partly soluble in chlorobenzene. The resulting green solution, chromatographed on alumina, gave two bands. The more strongly adsorbed was black; elution with pyridine gave a green solution which became purple on the addition of methanolic potassium hydroxide.

A repetition of the sublimation of a portion of (A) at 380—400°/0·5 mm., grinding the residue and again subliming, it gave the following yields: anthraquinone (0·0016 g.), unidentified red compound (0·0006 g.), 1 : 1′-dianthraquinonylamine (0·0089 g.), 1 : 2-phthaloylcarbazole (0·0029 g.), 1 : 2-7 : 8-diphthaloylcarbazole (0·0278 g.), and residue (0·0261 g.).

(*b*) 1 : 1′-Dianthraquinonylamine (2·0 g.), potassium hydroxide (20 g.), water (2 c.c.), and phenol (0·5 g.) heated and further treated as in (*a*) gave a brown solid (1·7 g.) which resembled (A) in composition. Vacuum-sublimation gave anthraquinone (0·0011 g.), unidentified red compound (0·0005 g.), 1 : 1′-dianthraquinonylamine (0·0008 g.), 1 : 2-phthaloylcarbazole (0·0016 g.), 1 : 2-7 : 8-diphthaloylcarbazole (0·0273 g.), and residue (0·0231 g.).

(*c*) Experiment (*b*) was repeated with the addition of zinc dust (0·75 g.) and omission of the phenol. Almost none of the product was soluble in aqueous potassium hydroxide (absence of alizarin) and on sublimation the sublimate was almost pure 1 : 1′-dianthraquinonylamine. Only a trace of diphthaloylcarbazole was present.

(*d*) 1 : 1′-Dianthraquinonylamine (5 g.) was recovered (4·6 g.) almost entirely unchanged after being heated with sodium hydroxide (50 g.) and water (5 c.c.) at 220° for 15 minutes;

alizarin was formed in very small amount. The same result was obtained when 1 : 1′-dianthraquinonylamine (0·2 g.), sodium hydroxide (2 g.), water (0·5 c.c.), and phenol (0·5 g.) were heated together at 220° for 30 minutes, and again when the last experiment was repeated with the addition of sodium chloride (cf. D.R.-P. 175,626). There was no formation of 1 : 2-7 : 8-diphthaloylcarbazole in any of these experiments.

(*e*) 1 : 1′-Dianthraquinonylamine (5 g.), heated at 220° for 5 hours with sodium hydroxide (50 g.), water (5 c.c.), and phenol (0·5 g.), with the addition of small successive amounts of water to keep the melt fluid, gave an acid (alizarin?), which dissolved in alkali with a violet colour, and a black alkali-insoluble solid (4·2 g.). After washing, drying, and heating at 440°/0·1 mm. a portion of the black solid yielded the following products: anthraquinone (0·0033 g.), 1 : 1′-dianthraquinonylamine (0·0014 g.), 1 : 2-phthaloylcarbazole (0·0048 g.), 1 : 2-7 : 8-diphthaloylcarbazole 0·0014 g.), and unsublimed residue (0·087 g.).

(*f*) Heated with sodium hydroxide (20 g.) and water (5 c.c.), 1 : 1′-dianthraquinonylamine (2 g.) remained largely unaltered until the temperature reached 250—260°. After 20 minutes at 280° 1·2 g. of product was obtained on addition to water. Sublimation of a portion gave anthraquinone (0·0018 g.), 1 : 1′-dianthraquinonylamine (0·0116 g.), 1 : 2-phthaloylcarbazole (0·003 g.), 1 : 2-7 : 8-diphthaloylcarbazole (0·0098 g.), and residue (0·0162 g.).

Degradation of 1 : 2-7 : 8-*Diphthaloylcarbazole by Potassium Hydroxide.*—(*a*) 1 : 2-7 : 8-Diphthaloylcarbazole (2 g.) was added to potassium hydroxide (20 g.) and water (2 c.c.) at 170—180° and then the temperature was raised to 220° during 30 minutes. After 15 minutes at 220° the melt was added to water (500 c.c.) and the yellow-brown solid was collected, and washed with 1% potassium hydroxide solution, and then with water. Finally it was dried (1·8 g.) and a portion was sublimed at 360—380°/0·5 mm. for 12 hours. The most volatile product was 1 : 2-phthaloylcarbazole (0·030 g.; m. p. 249—253°), identical with the compound prepared from 1-chloroanthraquinone and benzotriazole according to Ullmann and Illgen (*Ber.*, 1914, **47**, 380). 1 : 2-7 : 8-Diphthaloylcarbazole (0·001 g.) also sublimed; there was a non-volatile residue (0·009 g.).

(*b*) 1 : 2-7 : 8-Diphthaloylcarbazole (2 g.) was added to potassium hydroxide (40 g.) and water (4 c.c.) at 220°, and the mixture was stirred whilst the temperature was raised to 320° during 1 hour. Initially the reactants formed a yellow suspension, but the colour changed slowly to green. Finally a dark brown solution resulted. At this stage all the diphthaloylcarbazole, which was readily detected because it dissolved in alkaline dithionite solution with a red colour, had been decomposed. The product was added to water and the solution was filtered and acidified. A precipitate formed and this was collected, washed, and dried (0·75 g.). It was soluble in aqueous potassium carbonate. Heated with 200-mesh calcium oxide (7 g.) it yielded a sublimate of white plates, which, after collection, washing, and drying, had m. p. 226—230° (0·2 g.). Recrystallisation from aqueous alcohol gave the pure compound, m. p. 233—235°, not depressed by admixture with carbazole, m. p. 235—236°. It gave a green colour with sodium nitrite and concentrated sulphuric acid.

Fusion of 1 : 1′-*Dianthraquinonylamine with Cæsium Hydroxide.*—Aqueous solutions of cæsium sulphate (1·07 g.) and barium hydroxide (0·472 g.) were mixed, the precipitated barium sulphate removed, and the filtrate evaporated to dryness. Water (0·2 c.c.) was added to the residue and the resulting solution was heated to 150°. At this temperature 1 : 1′-dianthraquinonylamine (0·04 g.) was added. The mixture was then held at, successively, 150° (10 minutes), 160° (10 minutes), 200° (20 minutes). The product consisted of unaltered 1 : 1′-dianthraquinonylamine. In a second experiment 1 : 1′-dianthraquinonylamine (0·04 g.) was added to a similar preparation of cæsium hydroxide at 180°. The temperature was raised slowly to 220° and maintained for 20 minutes. Added to water (100 c.c.) the melt dissolved forming a brown solution. This was aerated for 4 hours and the brown precipitate was collected, washed, and dried (0·02—0·03 g.). Sublimation at 360°/0·5—1·0 mm. gave 1 : 2-7 : 8-diphthaloylcarbazole as the main product. Traces of 1 : 2-phthaloylcarbazole and 1 : 1′-dianthraquinonylamine were also present.

Action of Fused Potassium Hydroxide on 6 : 6′-*Di*mesobenzanthronylamine.—(*a*) Finely powdered 6 : 6′-di*meso*benzanthronylamine (1·0 g.) was added to potassium hydroxide (10 g.) and water (1 c.c.) at 180°. The temperature was raised slowly to 220°. Ammonia was evolved, vigorously at 220°. The reaction ceased after 25 minutes and the product was added to water. The suspension was acidified and the greenish-yellow solid was collected, washed, and dried (0·91 g.). Crystallised from benzene and then from acetic acid it gave needles, m. p. 176°, not depressed by admixture with 6-hydroxy*meso*benzanthrone, m. p. 177—178°.

(*b*) 6 : 6′-Di*meso*benzanthronylamine (4·0 g.) was added to potassium hydroxide (200 g.)

and water (20 g.) at 200°. The temperature was raised to 280° during an hour and then the product was isolated. It was a greenish-yellow solid (3·5 g.) which consisted of 6-hydroxy*meso*-benzanthrone (2·4 g.) and benzene-insoluble material (0·91 g.). The latter did not sublime at 360—400°/0·5—1·0 mm.; it decomposed above 400°.

Potassium Hydroxide Fusion of 1-*Aminoanthraquinone.*—The 1-aminoanthraquinone was first crystallised as the sulphate from sulphuric acid and then chromatographed from chlorobenzene on alumina. The amine (5 g.) was added to a melt of potassium hydroxide (50 g.) and water (5 c.c.) at 150°. The temperature was raised to 220° during 30 minutes and maintained for 15 minutes longer. The product added to water gave a brown suspension, and this was aerated for 24 hours. The dark brown precipitate (A) (4·6 g.; m. p. >360°) was separated from the solution which was then acidified. The resulting small precipitate was collected, washed, dried, dissolved in chlorobenzene, and then chromatographed on alumina. Three zones formed. The middle brick-red zone, extracted with acetic acid, gave orange needles, m. p. 288°, not depressed on admixture with alizarin. The product (A) extracted with acetic acid gave a deep green solution from which a blue solid (2·5 g.) separated on addition to water. The blue product extracted with chlorobenzene gave 1-aminoanthraquinone (0·5 g.; m. p. 252—253°), not depressed on admixture with authentic material. Prolonged extraction with chlorobenzene gave a green solution and this was chromatographed on alumina at 110°. Several zones formed; the main one was black and was the most strongly retained. The black zone extracted with acetic acid gave a solution from which a green precipitate (Found: C, 74·6; H, 3·2; N, 2·9%) (1·7 g.), m. p. 400°, separated on addition to water. This dissolved in concentrated sulphuric acid forming a red solution which became orange on the addition of a drop of formaldehyde solution but remained unchanged on addition of boric anhydride. The green substance dissolved in pyridine with the same colour; a purple colour developed on the addition of a drop of methyl-alcoholic potassium hydroxide, and the original colour was regenerated on further addition of water. It did not dissolve in 5% potassium hydroxide but a brown solution resulted on the addition of sodium dithionite; aeration reprecipitated the green substance. It was not affected by heating with acetic anhydride.

Potassium Hydroxide Fusion of 1-*Anilinoanthraquinone.*—1-Anilinoanthraquinone (5 g.) was added to potassium hydroxide (50 g.) and water (5 c.c.) at 170°. The temperature was raised slowly to 220° and maintained for 10 minutes. The black semi-solid product was added to water (200 c.c.), and the suspension was heated to boiling and aerated for 6 hours. Filtration afforded a purple solution and a solid. Acidification of the solution gave 0·85 g. of alizarin, m. p. 282—285° (288° after recrystallisation). Extraction of the solid with alcoholic potassium hydroxide solution gave an additional quantity of alizarin and a purple residue, melting range 120—140°. Crystallisation from alcohol gave unchanged 1-anilinoanthraquinone, m. p. 143—145°. Sublimation at 250°/0·1 mm. before crystallisation gave a trace of alizarin; 1 : 2-phthaloylcarbazole was absent.

Action of Aluminium Chloride on 1 : 1′-*Dianthraquinonylamine* (cf. B.I.O.S., *loc. cit.*).—An intimate mixture of anhydrous aluminium chloride (60 g.), 1 : 1′-dianthraquinonylamine (30 g.), and sodium chloride (7·5 g.) was heated at 165° for an hour and then at 250° for 30 minutes. The cooled product, added to water and heated with hydrochloric acid, gave 28 g. of insoluble black material (A), which still contained a small proportion of an aluminium compound (Found, in residue after further heating for 2 hours with hot, concentrated hydrochloric acid: Al, 0·3%). (A) adsorbed methylene-blue from an aqueous solution but did not reduce it. It did not reduce azobenzene at 100° (30 hours) or at 200° (6 hours), or bromanil in boiling acetic acid (3 hours). With a 5·14% solution of iodine in boiling benzene it gave a brownish-yellow product, not containing iodine. Heated with alkaline sodium hypochlorite, then with nitrobenzene, sodium hypochlorite, and potassium permanganate as described in the B.I.O.S. Report, 19 g. of (A) afforded a yellow product (8·5 g.). Crystallisation from nitrobenzene gave small, golden-yellow needles, which decomposed when heated above 400° and gave the same colour and absorption spectrum in concentrated sulphuric acid as the product obtained by the fusion of 1 : 1′-dianthraquinonylamine with potassium hydroxide (Figure).

Sublimed for 2 hours from a bath at 360—380°/0·5—0·8 mm. (A) afforded a more volatile band consisting of a small amount of crystalline 1 : 1′-dianthraquinonylamine and a crop of yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole. A separation carried out for 12 hours at 360° gave 1 : 2-7 : 8-diphthaloylcarbazole (43%), 1 : 1′-dianthraquinonylamine (1·1%), and unsublimed residue (48%).

Extracted with boiling dimethyl phthalate, (A) dissolved in part forming a yellow solution from which 1 : 2-7 : 8-diphthaloylcarbazole separated on cooling. The identity of the product

was confirmed by its absorption spectrum in sulphuric acid. Repeated extraction of (A) with dimethyl phthalate afforded a black, insoluble residue which did not dissolve in cold, concentrated sulphuric acid or in alkaline dithionite solution. Extracted for 12 hours with cold, concentrated sulphuric acid A (0·2962 g.) afforded 0·1430 g. (Found : C, 74·2; H, 3·6; N, 1·5%) of the residue.

Experiments on the Methylation of 1 : 1′-*Dianthraquinonylamine and its Derivatives.*—1 : 1′-Dianthraquinonylamine was recovered unaltered after 8 hours' heating with methyl toluene-*p*-sulphonate and potassium carbonate in *o*-dichlorobenzene. A similar results was obtained when the medium was mixed polychlorobenzenes, boiling range 220—240°, and the period of heating 48 hours.

4 : 4′-Dinitro-1 : 1′-dianthraquinonylamine was recovered mainly unchanged after 12 hours' heating in polychlorobenzenes with potassium carbonate and methyl toluene-*p*-sulphonate.

Similar negative results were obtained in attempts to *N*-methylate 2-*nitro*-1 : 1′-*dianthraquinonylamine*. This compound was prepared as follows.

1-Chloro-2-nitroanthraquinone (10 g.) and 1-aminoanthraquinone (10 g.) were heated under reflux in mixed polychlorobenzenes (80 c.c.; boiling range, 220—240°). Hydrogen chloride was liberated and the orange solution of the reactants slowly became dark bluish red. After 20 hours the product was cooled and added to alcohol (100 c.c.), and the red precipitate was washed with warm benzene. After further extraction with alcohol the residue (8 g.) crystallised from *o*-dichlorobenzene as bluish-red needles, m. p. 318° (Found : C, 70·8; H, 2·6; N, 5·6. $C_{28}H_{14}O_4N_2$ requires C, 70·9; H, 3·0; N, 5·9%). It dissolved in pyridine with a cherry-red colour changed to bright green on the addition of methyl-alcoholic potassium hydroxide. The green colour was stable towards the addition of a small proportion of water, but more water caused the regeneration ot the original red colour. It dissolved in concentrated sulphuric acid forming a bluish-green solution, changed to brown on the addition of boric acid, and rendered slightly bluer with formaldehyde. Heating for 30 minutes with alcohol containing 5% of hydrated sodium sulphide transformed 2-nitro-1 : 1′-dianthraquinonylamine into a blue product, m. p. >400°. This dissolved in alkaline dithionite forming a brown solution from which the original substance was reprecipitated on aeration. Contact with nitric acid rendered the blue compound yellow. Sublimed from a bath at 300—320°/1 mm. 2-nitro-1 : 1′-dianthraquinonylamine gave a purple product, m. p. 405—408° raised to 422—424° (Found : C, 72·0; H, 3·3; N, 4·7%) on crystallisation from pyridine. The purple solution in pyridine changed to pale blue on the addition of methyl-alcoholic potassium hydroxide.

1-Chloro-2-nitroanthraquinone (1·0 g.) and 1-methylaminoanthraquinone (1·0 g.) did not condense when heated in nitrobenzene (50 c.c.) for 20 hours. In the presence of cuprous chloride (0·5 g.) and potassium acetate (5·0 g.) 1-chloroanthraquinone (5·0 g.) and 1-methylaminoanthraquinone (5·0 g.) in nitrobenzene (50 c.c.) condensed with demethylation during 20 hours. The product (m. p. 378—381°; 8·4 g.) crystallised from the filtered nitrobenzene solution. The identity of the product with 1 : 1′-dianthraquinonylamine was confirmed by mixed m. p. and by the absorption spectrum in concentrated sulphuric acid.

6 : 6′-Di*meso*benzanthronylamine (1·0 g.) was recovered unaltered after 40 hours' heating with potassium carbonate (0·5 g.) and methyl toluene-*p*-sulphonate (2·0 g.) in *o*-dichlorobenzene (50 c.c.).

The authors thank the University of Leeds for the award of a Clothworkers' Research Scholarship and the Department of Scientific and Industrial Research for the award of a Maintenance Grant to one of them (C. R. T.).

CLOTHWORKERS' RESEARCH LABORATORY,
UNIVERSITY OF LEEDS.

[*Received, November 11th,* 1952.]