145. *Methyl Derivatives of* 1 : 4 : 5 : 8-*Tetra-aminoanthraquinone.*

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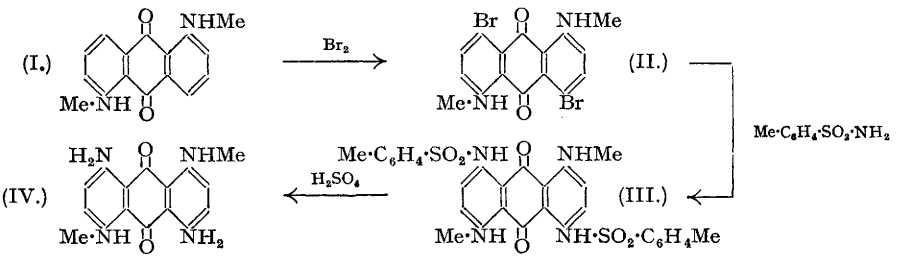
The synthesis of 4 : 8-*diamino*-1 : 5-*bismethylamino*- and of 4 : 5-*diamino*-1 : 8-*bismethylamino-anthraquinone*, and the attempted synthesis of 1 : 4 : 5 : 8-tetrakismethylaminoanthraquinone, are described.

The mixture of compounds obtained from the partial methylation of 1 : 4 : 5 : 8-tetra-aminoanthraquinone with methanol and sulphuric acid at 140° is stated to possess better dyeing properties for cellulose acetate rayon than does the original tetra-aminoanthraquinone (B.P. 391,859). Although these superior properties may be due to the mixture of very closely related compounds rather than to any one particular constituent, it was considered of interest to examine some of the more probable constituents in order to determine whether any one of them possessed outstanding characteristics, and also to obtain reference compounds for use in any attempted separation of the mixture into its constituents. Under the conditions used it is not considered that dimethylation of any one nitrogen atom would result (cf. D.R.-P. 288,825), and it is therefore necessary to consider only those derivatives of 1 : 4 : 5 : 8-tetra-amino-anthraquinone in which not more than one methyl group is attached to any single nitrogen atom.

Six such compounds can exist, namely, 4 : 5 : 8-triamino-1-methylamino-, 5 : 8-diamino-1 : 4-bismethylamino-, 4 : 8-diamino-1 : 5-bismethylamino-, 4 : 5-diamino-1 : 8-bismethylamino-, 8-amino-1 : 4 : 5-trismethylamino-, and 1 : 4 : 5 : 8-tetrakismethylamino-anthraquinone. Of these, 4 : 8-diamino-1 : 5-bismethylamino- and 4 : 5-diamino-1 : 8-bismethylamino-anthraquinone are probably formed on the methylation of 4 : 8-dinitro-1 : 5-diamino- and 4 : 5-dinitro-1 : 8-diamino-anthraquinone respectively with formaldehyde and formic acid followed by reduction with sodium sulphide (B.P. 282,853), although the actual identity of the products is not stated and neither melting points nor analytical data are recorded. 1 : 4 : 5 : 8-Tetrakismethylamino-anthraquinone is described in B.P. 442,726 as a dark blue crystalline solid, m. p. 308—310°, which was obtained by heating 4 : 8-diamino-1 : 5-dimethoxyanthraquinone with methylamine in ethanol at 180° for 5 hours. It is stated that the constitution of this compound as the tetrakismethylaminoanthraquinone is indicated by analysis, but no figures are recorded. This compound is possibly formed through 8-amino-1 : 4 : 5-trismethylaminoanthraquinone, which would show analytical figures very similar to those of the tetra-methylated compound. The same tetrakismethylaminoanthraquinone was described many years earlier (D.R.-P. 144,634) as a product of the action of methylamine on 4 : 8-dinitro-1 : 5-dichloroanthraquinone in pyridine at 160—170°, but again no melting point or analytical data were recorded and the product may have been a mixture. 4 : 5 : 8-*Triamino*-1-*methylamino*-, 5 : 8-*diamino*-1 : 4-*bismethylamino*-, and 8-*amino*-1 : 4 : 5-*trismethylamino-anthraquinone* have not been previously described. Of these six methyl derivatives of 1 : 4 : 5 : 8-tetra-aminoanthraquinone a successful synthesis of both 4 : 8-diamino-1 : 5-bismethylamino- and 4 : 5-diamino-1 : 8-bismethylamino-anthraquinone was achieved before the work was interrupted by the war.

4 : 8-*Diamino*-1 : 5-*bismethylaminoanthraquinone* (IV) was synthesised by the sequence of reactions represented below :



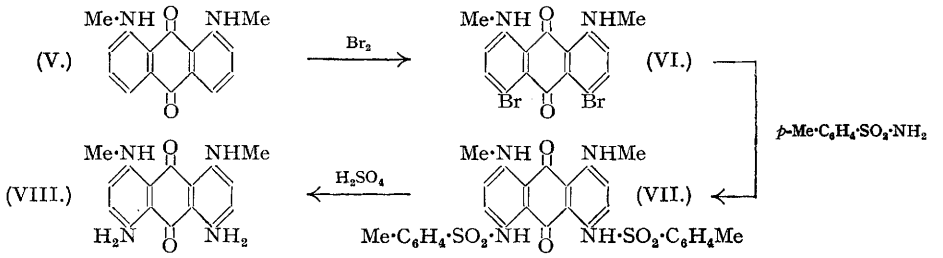
The bromination of 1 : 5-bismethylaminoanthraquinone (I) has been previously described (D.R.-P. 164,791), but preparations carried out by this published method gave only moderate yields of a product which proved difficult to purify and contained both unchanged material and a monobromo-compound. The required *dibromo*-compound (II) was eventually obtained in 80% yield by bromination in nitrobenzene solution in presence of sodium acetate. Condensation of (II) with *p*-toluenesulphonamide gave 4 : 8-*bis*-p-*toluenesulphonamido*-1 : 5-*bismethylamino-anthraquinone* (III) as a dark blue crystalline solid in over 90% yield, which on hydrolysis with

95% sulphuric acid gave 4 : 8-*diamino*-1 : 5-*bismethylaminoanthraquinone* (IV) in theoretical yield.

The 1 : 5-bismethylaminoanthraquinone (I) used as starting material in the above synthesis was obtained from anthraquinone-1 : 5-disulphonic acid and aqueous methylamine as described by Schmidt (*Ber.*, 1904, **37**, 70). Attempts were made to prepare (I) by the action of methylamine on the readily available 1 : 5-dichloroanthraquinone as mentioned in D.R.-P. 144,634, but on heating 1 : 5-dichloroanthraquinone for seven hours at 100° with a solution of methylamine in pyridine the product, obtained in good yield, was 5-*chloro*-1-*methylaminoanthraquinone*, which on acetylation gave 5-*chloro*-1-*acetmethylamidoanthraquinone*.

A possible alternative synthetic route to 4 : 8-diamino-1 : 5-bismethylaminoanthraquinone (IV) is suggested by the nitration of 1 : 5-bismethylaminoanthraquinone to give the 4 : 8-dinitro-derivative, as claimed in D.R.-P. 156,759, followed by reduction of the nitro-groups. Attempts to repeat the nitration of 1 : 5-bismethylaminoanthraquinone gave only a *tetranitro*-derivative (or mixture of tetranitro-derivatives), which decomposed at 220° with explosive violence, and, on reduction with sodium sulphide, gave a blue solid from which no pure compound could be isolated. Yet a third possible alternative route to (IV) is provided by the methylation of 4 : 8-dinitro-1 : 5-diaminoanthraquinone with formaldehyde and formic acid followed by reduction of the nitro-groups (B.P. 282,853). The attempted repetition of this process gave a product which appeared to contain mainly 1 : 4 : 5 : 8-tetra-aminoanthraquinone, and no (IV) was obtained.

4 : 5-*Diamino*-1 : 8-*bismethylaminoanthraquinone* (VIII) was synthesised from 1 : 8-dichloroanthraquinone which on being heated for seven hours at 180° with methylamine in pyridine gave 1 : 8-*bismethylaminoanthraquinone* (V). Bromination of the latter in nitrobenzene solution gave 4 : 5-*dibromo*-1 : 8-*bismethylaminoanthraquinone* (VI), which on being heated with *p*-toluenesulphonamide gave 4 : 5-*bis*-p-*toluenesulphonamido*-1 : 8-*bismethylaminoanthraquinone* (VII) in over 90% yield; this in turn was hydrolysed to give (VIII) in theoretical yield.



The preparation of 1 : 8-bismethylaminoanthraquinone (V) from 1 : 8-dichloroanthraquinone and from 1 : 8-dinitroanthraquinone by the action of methylamine in pyridine solution is mentioned in D.R.-P. 144,634, but no melting points or analyses are recorded for the product. The bromination of 1 : 8-bismethylaminoanthraquinone in pyridine solution is described in D.R.-P. 164,791, but again the product was not characterised.

The synthesis of 1 : 4 : 5 : 8-tetrakismethylaminoanthraquinone from 4 : 8-diamino-1 : 5-dimethoxyanthraquinone (obtained from 1 : 5-dimethoxyanthraquinone by nitration and reduction) has been described in B.P. 442,726. Attempts were made to prepare 1 : 5-dimethoxyanthraquinone both from anthraquinone-1 : 5-disulphonic acid (D.R.-P. 156,762; Barnett and Goodway, *Ber.*, 1930, **63**, 3048), and from 1 : 5-dinitroanthraquinone (D.R.-P. 77,818) by refluxing it with methanol and sodium hydroxide. Both methods gave poor yields, and whereas the product from 1 : 5-dinitroanthraquinone was bright red, that from the disulphonic acid was yellow. The red colour of the former was not removed on sublimation in high vacuum or by chromatographic adsorption on alumina, and both samples melted at the same temperature and showed no depression in melting point when mixed. At the time when the work had to be abandoned sufficient material had not been accumulated for nitration and reduction. Unsuccessful attempts were also made to condense 4 : 8-dibromo-1 : 5-bismethylaminoanthraquinone (II) with *p*-toluenesulphonmethylamide to give 4 : 8-bis-*p*-toluenesulphonmethylamido-1 : 5-bismethylaminoanthraquinone, which should yield the tetrakismethylaminoanthraquinone on hydrolysis. In similar manner the attempted methylamination of (II) with methylamine in pyridine at 160—170° yielded a product from which no pure compound could be isolated. It was also found impossible to methylate 4 : 8-bis-*p*-toluenesulphonamido-1 : 5-bismethylaminoanthraquinone (III) with methyl sulphate in nitrobenzene at

155—160°, although Waldman (*J. pr. Chem.*, 1937, **147**, 326) had previously reported successful methylation reactions of this type. The attempted methylation of 1 : 4 : 5 : 8-tetra-acetamidoanthraquinone also failed.

Experimental.

5-Chloro-1-methylaminoanthraquinone.—A mixture of 1 : 5-dichloroanthraquinone (25 g.) and pyridine (120 c.c.) containing methylamine (11 g.) was heated in a pressure bottle at 110° for 8 hours and poured into water (600 c.c.). The crude chloromethylaminoanthraquinone separated as a dark red solid which was washed twice with water and dried (24 g.). After sublimation in high vacuum at 135° and crystallisation from glacial acetic acid, *5-chloro-1-methylaminoanthraquinone* * was obtained in red needles with a golden lustre, m. p. 194—196° (Found: C, 66·5; H, 3·9. $C_{15}H_{10}O_2NCl$ requires C, 66·3; H, 3·7%). The solid formed bluish-red solutions in pyridine and in 2-methoxyethanol, and dissolved in hot concentrated hydrochloric acid and in cold concentrated sulphuric acid to give colourless solutions. The base (5 g.) was acetylated by boiling it for 2 hours with acetic anhydride (25 c.c.) containing 2 drops of concentrated sulphuric acid. The crystalline deposit which separated on cooling was collected, washed with ethanol, and dried (4·3 g.). Crystallisation from boiling 2-methoxyethanol gave *5-chloro-1-acetmethylamidoanthraquinone* in brownish-yellow needles, m. p. 201—202° (decomp.) (Found: C, 64·9; H, 3·9. $C_{17}H_{12}O_3NCl$ requires C, 65·1; H, 3·9%).

4 : 8-*Dibromo*-1 : 5-*bismethylaminoanthraquinone* (II).—(*a*) A stirred suspension of 1 : 5-bismethylamino anthraquinone (26·6 g.) and fused sodium acetate (20 g.) in nitrobenzene (100 c.c.) was heated at 100° and then allowed to cool to 20° with stirring. Bromine (11·5 c.c.) was added at this temperature during 2 hours with stirring. After standing over-night the precipitate was collected, washed with ethanol (70 c.c.), boiled with water (1000 c.c.), filtered off, and washed with hot water. The residue (36·5 g.) was extracted with 20% hydrochloric acid (450 c.c.) to remove unchanged 1 : 5-bismethylaminoanthraquinone. The insoluble residue was washed with hot water and dried (33 g.). Crystallisation from chlorobenzene gave 4 : 8-*dibromo*-1 : 5-*bismethylaminoanthraquinone* * in small reddish-brown crystals which decomposed at 212—215° (Found: C, 45·2; H, 3·1. $C_{16}H_{12}O_2N_2Br_2$ requires C, 45·3; H, 2·85%). This compound gave red solutions in organic solvents but dissolved in cold concentrated sulphuric acid to form a nearly colourless solution which on dilution with much water deposited the free base as a red solid.

(*b*) (cf. D.R.-P. 164,791.) Bromine (40 g.) was added cautiously to a suspension of 1 : 5-bismethylaminoanthraquinone (25 g.) in pyridine (1000 c.c.) at 40° and the resulting mixture was heated on the steam-bath for 3 hours. Methylated spirits (500 g.) and water (300 c.c.) were added and the mixture was allowed to cool over-night. After a day at 0° the precipitated brown solid was collected and dried (32 g.). After removal of unchanged starting material as before, the residue (20 g.) was crystallised from chlorobenzene and gave 4 : 8-dibromo-1 : 5-bismethylaminoanthraquinone identical with that prepared by method (*a*).

4 : 8-*Bis*-p-*toluenesulphonamido*-1 : 5-*bismethylaminoanthraquinone* (III).—A mixture of 4 : 8-dibromo-1 : 5-bismethylaminoanthraquinone (12·7 g.), *p*-toluenesulphonamide (10·8 g.), anhydrous potassium carbonate (4·5 g.), copper acetate (0·4 g.), and nitrobenzene (80 c.c.) was heated at 170—190° for 4 hours. Reaction began at 140—150° and the mixture became blue. After removal of the nitrobenzene by distillation with steam the residue was washed with hot 90% ethanol and boiled with successive portions of water until free from inorganic salts. Crystallisation of the residual dark blue solid (17 g.) from either chlorobenzene or nitrobenzene gave 4 : 8-*bis*-p-*toluenesulphonamido*-1 : 5-*bismethylaminoanthraquinone* in prisms with a bronze-red lustre, which did not melt below 330° (Found: C, 59·6; H, 5·0. $C_{30}H_{28}O_6N_4S_2$ requires C, 59·6; H, 4·7%). This compound gave a blue solution in nitrobenzene and dissolved in cold concentrated sulphuric acid to give a very dark red solution from which excess of water precipitated the blue base.

4 : 8-*Diamino*-1 : 5-*bismethylaminoanthraquinone* (IV).—A solution of 4 : 8-bis-*p*-toluenesulphonamido-1 : 5-bismethylaminoanthraquinone (11·7 g.) in 95% sulphuric acid (120 c.c.) was allowed to stand over-night at room temperature, after which it was heated on the steam-bath for 3 hours. The cold solution was poured into excess of water, neutralised with ammonia, and filtered, and the solid (6 g.) was washed well with hot water. Crystallisation from chlorobenzene, *o*-dichlorobenzene, or nitrobenzene gave 4 : 8-*diamino*-1 : 5-*bismethylaminoanthraquinone* * as a dark blue microcrystalline solid with an intense bronze-red lustre, m. p. 253—255° (Found: C, 64·6; H, 5·45. $C_{16}H_{16}O_2N_4$ requires C, 64·85; H, 5·4%). In concentrated sulphuric and hydrochloric acids the compound gave red solutions which on dilution with water deposited the reddish salt of the base. On further dilution hydrolysis to the free base occurred. The base gave intense blue solutions in organic solveents.

Nitration of 1 : 5-*Bismethylaminoanthraquinone* (cf. D.R.-P., 156,759).—1 : 5-Bismethylaminoanthraquinone (10 g.) was added slowly to stirred nitric acid (*d* 1·42; 100 c.c.), the temperature being maintained below 30°. The yellow solution changed to bluish-red and finally to violet, and reddish-violet crystals began to separate. After being stirred for 4 hours after the last addition of base, the mixture was poured into water (800 c.c.) and filtered. The precipitate was extracted with hot 20% hydrochloric acid and finally with water until free from acid. The resulting reddish-violet solid (13·3 g.) had m. p. 215° (decomp.), but decomposed with explosive violence when heated in quantity. After crystallisation from amyl alcohol–ethanol the *tetranitro*-derivative had m. p. 220° (decomp.) (Found: C, 43·85; H, 2·6; N, 18·8. $C_{16}H_{10}O_{10}N_6$ requires C, 43·1; H, 2·3; N, 18·8%). Reduction of the tetranitro-compound with aqueous sodium sulphide gave a mixture of bases from which no pure compounds were isolated.

Methylation of 4 : 8-*Dinitro*-1 : 5-*diaminoanthraquinone* (cf. B.P. 282,853).—4 : 8-Dinitro-1 : 5-diaminoanthraquinone was heated with a mixture of formic acid and aqueous formaldehyde, as described in

* Compounds marked with an asterisk have been previously mentioned in patent literature, but no melting points or analytical data have been recorded.

B.P. 282,853. The product (15 g.) in suspension in water (600 c.c.) was reduced with a hot solution of sodium sulphide (90 g.) in water (300 c.c.). The resulting blue solid was well washed with hot water and melted at 270—280°. No pure compounds could be isolated.

1 : 8-*Bismethylaminoanthraquinone* (V) (cf. D.R.-P. 144,634).—1 : 8-Dichloroanthraquinone (50 g.) and a solution of methylamine (29 g.) in pyridine (200 c.c.) were heated in an autoclave at 160—180° for 7 hours and then poured into water; a brown solid separated, and was collected, washed with water, and dried (37 g.). After sublimation in high vacuum at 120° and recrystallisation from glacial acetic acid, pyridine, or 2-methoxyethanol, 1 : 8-*bismethylaminoanthraquinone* * was obtained in purple prisms with a green lustre, m. p. 215—217° (Found : C, 72·3; H, 5·2. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3%). In cold concentrated sulphuric and hydrochloric acids, the base gave almost colourless solutions from which, on dilution with water, the free base separated as a purple precipitate. The base gave bluish-red solutions in most organic solvents. When methylamination was attempted at 100° the reaction was incomplete, and considerable difficulty was experienced in isolating 1 : 8-bismethylaminoanthraquinone in pure form.

4 : 5-*Dibromo*-1 : 8-*bismethylaminoanthraquinone* (VI).—(*a*) A stirred suspension of 1 : 8-bismethylaminoanthraquinone (15 g.) and fused sodium acetate (12 g.) in nitrobenzene (60 c.c.) was heated on the steam-bath and then cooled to 20°. Bromine (7 c.c.) was added at this temperature during 2 hours with stirring. Stirring was continued for a further 8 hours, and after standing over-night the precipitate was collected, and washed with ethanol and then with hot water until free from bromide (yield, 11·2 g.). Crystallisation from chlorobenzene or 2-methoxyethanol gave 4 : 5-*dibromo*-1 : 8-*bismethylaminoanthraquinone* * in brownish-violet prisms with a greenish-golden lustre, which decomposed at 228—230° (Found : C, 45·2; H, 3·25. $C_{16}H_{12}O_2N_2Br_2$ requires C, 45·3; H, 2·85%). Dilution of the nitrobenzene mother liquor with ethanol precipitated impure 1 : 8-bismethylaminoanthraquinone (8 g.). The dibromo-compound gave an almost colourless solution in concentrated sulphuric acid, and dilution with much water precipitated the free base as a reddish-violet solid.

(*b*) (cf. D.R.-P. 164,791.) Bromine (6·4 c.c.) was added to a suspension of 1 : 8-bismethylaminoanthraquinone (12·4 g.) in pyridine (500 c.c.) at 40° after which the mixture was heated for 3 hours on the steam-bath. Methylated spirit (300 c.c.) was added, and the mixture was allowed to stand over-night. The brownish-violet crystalline deposit was collected (6·1 g.) and recrystallised from chlorobenzene. 4 : 5-Dibromo-1 : 8-bismethylaminoanthraquinone (5·4 g.) was obtained, identical with that prepared by method (*a*).

4 : 5-*Bis*-p-*toluenesulphonamido*-1 : 8-*bismethylaminoanthraquinone* (VII).—A mixture of 4 : 5-dibromo-1 : 8-bismethylaminoanthraquinone (8·5 g.), *p*-toluenesulphonamide (7·5 g.), anhydrous potassium carbonate (3 g.), copper acetate (0·4 g.), and nitrobenzene (60 c.c.) was heated at 180—190° for 4 hours. Reaction began at 140—150° and the mixture became blue. The nitrobenzene was removed with steam and the residue was twice extracted with boiling water and then washed with hot water until free from inorganic salts (yield, 11 g.). Crystallisation from nitrobenzene gave 4 : 5-*bis*-p-*toluenesulphonamido*-1 : 8-*bismethylaminoanthraquinone* in blue prisms with a bronze-gold lustre which decomposed at 300—303° (Found : C, 59·7; H, 5·0. $C_{30}H_{28}O_6N_4S_2$ requires C, 59·6; H, 4·7%). This compound gave blue solutions in organic solvents and dissolved in cold concentrated sulphuric acid to give a deep red solution from which addition of excess water precipitated the blue base.

4 : 5-*Diamino*-1 : 8-*bismethylaminoanthraquinone* (VIII).—A solution of 4 : 5-bis-*p*-toluenesulphonamido-1 : 8-bismethylaminoanthraquinone (10·1 g.) in 95% sulphuric acid (100 c.c.) was allowed to stand over-night at room temperature and then heated on the steam-bath for 3 hours. The cold red solution was poured into water, neutralised with ammonia, and filtered. The blue residue (5 g.) was washed well with hot water. Crystallisation from chlorobenzene or nitrobenzene gave 4 : 5-*diamino*-1 : 8-*bismethylaminoanthraquinone* * as a dark blue microcrystalline solid with a bronze-red lustre, m. p. 227—229° (Found : C, 64·7; H, 5·4. $C_{16}H_{16}O_2N_4$ requires C, 64·85; H, 5·4%). The base gave deep red solutions in concentrated sulphuric or hydrochloric acids. Dilution precipitated first the reddish salt and then by hydrolysis the blue free base, which gave blue solutions in organic solvents.

Attempted Preparations of 1 : 4 : 5 : 8-*Tetrakismethylaminoanthraquinone.*—(*a*) A mixture of 4 : 8-dibromo-1 : 5-bismethylaminoanthraquinone (8·5 g.), *p*-toluenesulphonmethylamide (7·4 g.), anhydrous potassium carbonate (3 g.), copper acetate (0·4 g.), and nitrobenzene (70 c.c.) was heated slowly to 170—190° and maintained at this temperature for 4 hours. A vigorous reaction appeared to set in at 140—150°, when the mixture turned blue. The nitrobenzene was removed with steam and the residue was extracted successively with boiling ethanol and boiling water. No pure product could be obtained from the residue (7 g.), which softened at 160° but did not melt below 330°, and attempted hydrolysis with 95% sulphuric acid gave a product which melted above 330°. The m. p. of 1 : 4 : 5 : 8-tetrakismethylaminoanthraquinone given in B.P. 442,726 is 308—310°.

(*b*) A mixture of 4 : 8-dibromo-1 : 5-bismethylaminoanthraquinone (20 g.), copper acetate (0·4 g.), and pyridine (100 c.c.) containing methylamine (10 g.) was heated in an autoclave at 160—170° for 9 hours. The cold mixture was filtered and the residue well washed with hot water and dried (4·95 g.). Addition of water to the pyridine mother liquor precipitated more solid, which was well washed and dried (11·5 g.). No pure compound could be isolated from these products. A similar reaction carried out at 90—100° gave a product (10·2 g., m. p. 284—286°) from which no pure compound could be obtained by fractional precipitation by addition of water to its solution in concentrated sulphuric acid.

(*c*) A mixture of 4 : 8-bis-*p*-toluenesulphonamido-1 : 5-bismethylaminoanthraquinone (6 g.), methyl sulphate (3 g.), anhydrous potassium carbonate (3 g.), and nitrobenzene (50 c.c.) was heated at 155—160° for 4 hours. Nitrobenzene was removed with steam and the residue washed with ethanol and hot water. Recrystallisation from nitrobenzene gave a product (3·6 g.) which did not melt below 330°. Hydrolysis with 95% sulphuric acid gave only 4 : 8-diamino-1 : 5-bismethylaminoanthraquinone.

(*d*) A mixture of 1 : 4 : 5 : 8-tetra-aminoanthraquinone (20 g.), acetic acid (60 c.c.), and acetic anhydride (60 c.c.) was boiled under reflux for 2 hours. The dark red mixture was poured into water (700 c.c.) and the precipitate collected, washed, and dried (28·5 g.). Several recrystallisations from

nitrobenzene gave 1 : 4 : 5 : 8-tetra-acetamidoanthraquinone in short thick crystals with a greenish-golden lustre, m. p. 315—320° (Found : C, 60·3; H, 4·9. Calc. for $C_{22}H_{20}O_6N_4$: C, 60·5; H, 4·6%). Noelting and Wortmann (*Ber.*, 1906, **39**, 646) state that the compound does not melt below 330°. The tetra-acetyl derivative (5 g.), dry benzene (45 c.c.), and sodium (1 g.) were heated on the steam-bath under reflux for 3 hours. When cold, methyl sulphate (4·5 c.c.) was added and the mixture refluxed for 3 hours. After addition of ethanol the mixture was filtered, and the residue, washed successively with alcohol and hot water, proved to be unchanged 1 : 4 : 5 : 8-tetra-acetamidoanthraquinone. In a second experiment the tetra-acetyl derivative (5 g.), anhydrous potassium carbonate (6·5 g.), methyl sulphate (6·4 g.), and nitrobenzene (40 c.c.) were heated at 150—160° for 5 hours. Nitrobenzene was removed with steam and the residue washed well with hot water. Several crystallisations from nitrobenzene gave a solid which did not melt below 330° (Found : C, 63·7; H, 4·6%), and since it gave blue solutions in organic solvents it was probably a mixture of *N*-methyl derivatives of 1 : 4 : 5 : 8-tetra-aminoanthraquinone.

1 : 5-*Dimethoxyanthraquinone.*—(*a*) (cf. D.R.-P. 156,762; Barnett and Goodway, *loc. cit.*). A mixture of sodium anthraquinone-1 : 5-disulphonate (50 g.), methanol (500 c.c.), and 30% aqueous sodium hydroxide (125 c.c.) was boiled under reflux for 80 hours. The mixture was added to water (2000 c.c.), and the precipitate collected, washed, and dried (34 g.). Boiling ethanol extracted crude 1 : 5-dimethoxyanthraquinone (12 g.) which after several crystallisations from the same solvent was obtained in yellow needles, m. p. 234—236° (Found : C, 71·6; H, 4·65. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5%). Freund and Achenbach (*Ber.*, 1910, **43**, 3260) gave m. p. 232—234°, Attree and Perkin (*J.*, 1931, 144), m. p. 236—238°, and Barnett and Goodway (*loc. cit.*), m. p. 241°.

(*b*) (cf. D.R.-P. 77,818.) A mixture of 1 : 5-dinitroanthraquinone (50 g.), sodium hydroxide (20 g.), and dry methanol (350 c.c.) was boiled under reflux for 50 hours. After removal of most of the methanol by distillation the residue was extracted with water. The residue (41 g.) was crystallised from glacial acetic acid with charcoal, and after sublimation in high vacuum followed by further crystallisation from ethanol gave 1 : 5-dimethoxyanthraquinone in red needles (10·2 g.), m. p. 233—235° (Found : C, 71·5; H 4·6. Calc. for $C_{16}H_{12}O_4$: C, 71·6; H, 4·5%). The m. p. was unchanged on admixture with the yellow needles prepared by method (*a*).

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