Cyclisation of Benzamido-derivatives of 1 : 1′-*Dianthraquinonylamine to Derivatives of* 1 : 2-7 : 8-*Diphthaloylcarbazole.*

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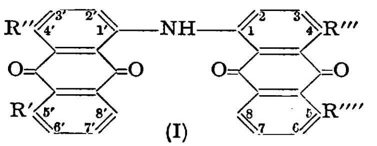
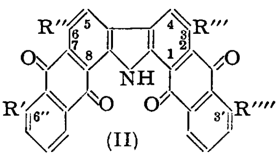
On being heated with concentrated sulphuric acid the 4 : 4′-, 4 : 5′-, and 5 : 5′-dibenzamido-derivatives of 1 : 1′-dianthraquinonylamine are transformed into dibenzamido-derivatives of 1 : 2-7 : 8-diphthaloylcarbazole.

IN 1910 Mieg (G.P. 239,544) showed that on being heated with concentrated sulphuric acid at 30—40° 4 : 5′-dibenzamido-1 : 1′-dianthraquinonylamine (I; R′ = R‴ = NHBz, R″ = R⁗ = H) gave a brown colouring matter, and that similar treatment of the 4 : 4′-isomer (I; R″ = R‴ = NHBz, R′ = R⁗ = H) gave an olive dye. Mieg regarded his products as acridines formed by dehydration, but it was found later (G.P. 464,292) that the olive dye resulted also from 1 : 2-7 : 8-diphthaloylcarbazole (II) by nitration, reduction, and benzoylation. Thereafter both the olive and the brown dye and an analogous orange-yellow product from 5 : 5′-dibenzamido-1 : 1′-dianthraquinonylamine (I; R′ = R′′′′ = NHBz, R′′ = R′′′ = H) (G.P. 239,544; Swiss P. 115,114) came to be regarded as derivatives of carbazole.



(I)



(II)

In the present experiments the three dibenzamido-derivatives of 1 : 1′-dianthraquinonylamine have been prepared in pure condition, further characterised, and converted into the products described in the patents mentioned. The final products have been described in greater detail, analysed, and then converted by removal of benzoyl groups and resulting amino-groups into 1 : 2-7 : 8-diphthaloylcarbazole (II; R′ = R′′ = R′′′ = R′′′′ = H), identical with the compound prepared by Bradley and Thitchener (*J.*, 1953, 1085). The carbazole structure of the three colouring matters is thus confirmed, and with this the remarkable dehydrogenation and cyclisation of substituted 1 : 1′-dianthraquinonylamines by means of warm concentrated sulphuric acid.

The three dibenzamido-derivatives of 1 : 1′-dianthraquinonylamine were prepared essentially by the methods of G.P. 162,824 and 220,581. They were debenzoylated by hot phosphoric acid; there was no evidence of cyclisation in this reaction. Deamination was by diazotization and treatment with hypophosphorous acid.

Heating with phosphoric acid provides a convenient means of hydrolysing many *N*-acylaminoanthraquinones; several examples are given in the Experimental portion.

EXPERIMENTAL

5 : *5′-Dibenzamido-*1 : *1′-dianthraquinonylamine.*—A sample of 1-amino-5-benzamidoanthraquinone had m. p. 249° after crystallisation from chlorobenzene (Found: N, 8·05. Calc. for $C_{21}H_{14}O_3N_2$: N, 8·19%). Hefti (*Helv. Chim. Acta*, 1931, **14**, 1404) records m. p. 244—245°. 1-*Benzamido-5-chloroanthraquinone* crystallised from chlorobenzene as golden-yellow needles, m. p. 218° (Found: N, 3·9; Cl, 9·7. $C_{21}H_{12}O_3NCl$ requires N, 3·9; Cl, 9·8%). 5 : *5′-Dibenzamido-*1 : *1′-dianthraquinonylamine,* prepared by heating 1-amino-5-benzamidoanthraquinone with 1-benzamido-5-chloroanthraquinone in nitrobenzene with copper chloride, sodium acetate, and sodium carbonate, crystallised (Soxhlet) from chlorobenzene in fine, dark red needles, m. p. > 360° (Found: C, 75·6; H, 3·7; N, 6·3. $C_{42}H_{25}O_6N_3$ requires C, 75·6; H, 3·8; N, 6·3%). The solution in concentrated sulphuric acid was green; addition of 40% formaldehyde solution changed the colour to blue. The red solution in pyridine became yellow-brown on the addition of methanolic potassium hydroxide.

3′ : *6′′-Dibenzamido-*1 : 2-7 : *8-diphthaloylcarbazole* (II; R′ = R′′′′ = NHBz, R′′ = R′′′ = H).—The orange product obtained by heating 5 : 5′-dibenzamido-1 : 1′-anthraquinonylamine with concentrated sulphuric acid at 30—35° was heated with aqueous sodium dichromate solution, then with sodium hydrogen sulphite, as described in B.I.O.S. Final Report, No. 1493, p. 17 (London, H.M.S.O.). Finally, it was washed, dried, and crystallised from 1 : 2 : 4-trichlorobenzene (Found: C, 76·1, 75·6; H, 4·3, 2·9; N, 6·1. Calc. for $C_{42}H_{23}O_6N_3$: C, 75·8; H, 3·5; N, 6·3%). The purified derivative was very sparingly soluble in dimethyl phthalate and in 1 : 2 : 4-trichlorobenzene. Absorption max. in " AnalaR " sulphuric acid: 323 (ε 5·08 × 10^4), 640 mμ (ε 5·97 × 10^4). The blue solution in this medium was initially unchanged by the addition of 40% aqueous formaldehyde but a grey violet colour developed after a few minutes. A solution in trichlorobenzene gave a single, strongly absorbed, orange band when chromatographed on alumina.

Another preparation of the colouring matter in which the treatment with dichromate and bisulphite was omitted and the product was crystallised from dimethyl phthalate gave the same result.

Hydrolysis.—The foregoing compound (0·54 g.) was heated at 180—190° for 7 hr. with syrupy phosphoric acid (30 c.c.; *d* 1·75), which had been heated previously to 240° until foaming ceased. The resulting solution was cooled and added to water, and the insoluble portion was collected and washed in turn with water, aqueous sodium carbonate, and water, and then dried (0·38 g.). The 3′ : 6″-diamino-1 : 2-7 : 8-diphthaloylcarbazole separated from 1 : 2 : 4-trichlorobenzene as a dull, reddish-orange solid, which sublimed *in vacuo* to give a single band of the same colour.

Deamination.—A solution of the diamine (1·2 g.) in 96% sulphuric acid (20 c.c.) was added at 0—5° to one of nitrosylsulphuric acid prepared from sodium nitrite (0·4 g.) and 96% sulphuric acid (20 c.c.). After being stirred for 1·5 hr. the resulting solution was added to 200 g. of crushed ice. The bisdiazonium salt separated in part, leaving an orange solution. After 0·5 hr. hypophosphorous acid (20 c.c. of 30%) was slowly added (0·5 hr.) at −5° and then stirring was continued for 2·5 hr. After 12 hr. at 0° the insoluble product was collected, washed neutral, dried (1·1 g.), and sublimed *in vacuo*. The orange-yellow needles formed (Found : C, 78·7; H, 3·2; N, 3·3. Calc. for $C_{28}H_{13}O_4N$: C, 78·7; H, 3·0; N, 3·3%) showed the following absorption maxima in concentrated sulphuric acid : 270 (ε $3·34 \times 10^4$) and 510 mμ (ε = $1·97 \times 10^4$), and were shown by direct comparison to be identical with 1 : 2-7 : 8-diphthaloylcarbazole (Found, in authentic sample : C, 78·8; H, 3·1; N, 3·5%. Absorption in concentrated sulphuric acid : max. 270 (ε $3·41 \times 10^4$), 510 mμ (ε $2·15 \times 10^4$).

4 : 5′-*Dibenzamido*-1 : 1′-*dianthraquinonylamine.*—1-Benzamido-4-chloroanthraquinone crystallised from chlorobenzene as golden-yellow needles, m. p. 238° (Found : N, 3·9; Cl, 9·4. Calc. for $C_{21}H_{12}O_3NCl$: N, 3·9; Cl, 9·8%); Bedekar, Tilak, and Venkataraman (*Proc. Indian Acad. Sci.*, 1948, **28**, 249) state m. p. 240°. When it was condensed with 1-amino-5-benzamidoanthraquinone by the method adopted for the preparation of the 5 : 5′-isomer the result was a dark solid. The 4 : 5′-*dibenzamido-amine* separated from nitrobenzene or *o*-dichlorobenzene as granules having a slightly bronzy lustre, but well-defined crystals were not obtained. The olive-green solution in concentrated sulphuric acid became darker and blue-green in colour on the addition of formaldehyde. The wine-red solution in pyridine became grey with a drop of methyl-alcoholic potassium hydroxide (Round : C, 73·6; H, 3·8; N, 6·5. $C_{42}H_{25}O_6N_3$ requires C, 75·6; H, 3·8; N, 6·3%).

3 : 6″-*Dibenzamido*-1 : 2-7 : 8-*diphthaloylcarbazole* (II; R′ = R‴ = NHBz, R″ = R⁗ = H).—The foregoing product was stirred for 7 hr. at 20—25° with 96% sulphuric acid and 20% oleum. The resulting solution was added to water containing sodium chlorate and heated as described in B.I.O.S. Final Report, No. 1493, p. 13. The insoluble 3 : 6″-*dibenzamido-carbazole* furnished a red-brown powder which was extremely sparingly soluble in 1 : 2 : 4-trichlorobenzene or dimethyl phthalate (Found : C, 75·2; H, 3·7; N, 6·0. $C_{42}H_{23}O_6N_3$ requires C, 75·8; H, 3·5; N, 6·3%). A solution in concentrated sulphuric acid showed absorption max. at 343 (ε $4·47 \times 10^4$), 560 (ε $3·54 \times 10^4$), and 605 mμ (ε $3·82 \times 10^4$). The bluish-red solution remained unaltered at first on the addition of formaldehyde but after a few minutes it became grey. The same product was obtained when 4 : 5′-dibenzamido-1 : 1′-dianthraquinonylamine was treated with 98% sulphuric acid only, the subsequent treatment with sodium chlorate being omitted. Absorption in concentrated sulphuric acid : max. 343 (ε $4·27 \times 10^4$), 560 (ε $3·48 \times 10^4$), and 605 mμ (ε $3·95 \times 10^4$).

Hydrolysis.—Following the procedure used for the orange isomer, the above red-brown colouring matter (0·88 g.) was heated for 7 hr. at 180—190° with syrupy phosphoric acid (30 c.c.; *d* 1·75). Benzoic acid sublimed. The resulting diamine was a dark brown solid (0·61 g.) which was very sparingly soluble in 1 : 2 : 4-trichlorobenzene. It sublimed with difficulty *in vacuo* with formation of purplish-black needles.

Deamination.—A solution of the diamine (0·6 g.) in concentrated sulphuric acid (20 c.c.) was diazotized as described above by means of nitrosylsulphuric acid prepared from sodium nitrite (0·2 g.) and concentrated sulphuric acid (20 c.c.). The precipitated bisdiazonium salt was reduced as above. The product (0·55 g.) was a light brown powder which dissolved in hot 1 : 2 : 4-trichlorobenzene with a yellow colour and on sublimation gave orange-yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole (Found : N, 3·5. Calc. for $C_{28}H_{13}O_4N$: N, 3·3%). A solution in concentrated sulphuric acid exhibited max. at 270 (ε $3·41 \times 10^4$) and 510 mμ (ε $2·02 \times 10^4$).

4 : 4′-*Dibenzamido*-1 : 1′-*dianthraquinonylamine.*—The crude product obtained by condensing 1-benzamido-4-chloroanthraquinone with 1-amino-4-benzamidoanthraquinone (Il'inski and Saikin, *Zentr.*, 1934, I, 1041) was washed with alcohol, and extracted in turn with hot dilute ammonia and then water. Crystallisation from nitrobenzene gave the 4 : 4′-*dibenzamido-amine* as dark, lustrous needles which were green by transmitted and purple by reflected light (Found : C, 75·4; H, 3·8; N, 6·3. $C_{42}H_{25}O_6N_3$ requires C, 75·6; H, 3·8; N, 6·3%). This product was identical with the compound prepared by the following means. 1-Aminoanthraquinone was condensed with 1-chloroanthraquinone to give 1 : 1′-dianthraquinonylamine

(Found : C, 78·7; H, 3·6; N, 3·4. Calc. for $C_{28}H_{15}O_4N$: C, 78·3; H, 3·5; N, 3·3%). Nitration according to Eckert and Steiner (*Monatsh.*, 1913, **123**, IIb, 625) gave a red-brown dinitro-compound which crystallised from nitrobenzene in orange needles (Found : C, 64·6; H, 3·4; N, 7·8. Calc. for $C_{28}H_{13}O_8N_3$: C, 64·7; H, 2·5; N, 8·1%). Reduction with sodium sulphide gave the diamino-compound, and this crystallised from *o*-dichlorobenzene in very dark purple, almost black, plates (Found : C, 72·4; H, 3·5; N, 8·7. Calc. for $C_{28}H_{17}O_4N_3$: C, 73·2; H, 3·7; N, 9·2%). On being heated with benzoyl chloride (1 c.c.) in *o*-dichlorobenzene (15 c.c.) at 150° for 3 hr. the diamine (1 g.) gave 1·45 g. of 4 : 4'-dibenzamido-1 : 1'-dianthraquinonylamine, which after crystallisation from *o*-dichlorobenzene was identical (Found : N, 6·5%) with the compound obtained by condensing 1-benzamido-4-chloroanthraquinone with 1-amido-4-benzamidoanthraquinone.

3 : 6-*Dibenzamido*-1 : 2-7 : 8-*diphthaloylcarbazole* (II; R'' = R''' = NHBz, R' = R'''' = H).—The *product* obtained by stirring 4 : 4'-dibenzamido-1 : 1'-dianthraquinonylamine with concentrated sulphuric acid at 25—30°, and addition to aqueous sodium chlorate (B.I.O.S. Final Report No. 1493, p. 31) was a dark blue-green powder. Crystallisation from dimethyl phthalate gave minute, dark blue-green needles (Found : C, 75·3; H, 3·5; N, 6·4. $C_{42}H_{23}O_6N_3$ requires C, 75·8; H, 3·5; N, 6·3%). A solution in concentrated sulphuric acid showed max. at 268 (ε 4·42 × 10^4), 365 (ε 5·25 × 10^4), 380 (ε 5·2 × 10^4), 550—554 (ε 3·49 × 10^4), and 590 mμ (ε 3·71 × 10^4). This derivative is less soluble in boiling diethyl phthalate (0·07%) than in dimethyl phthalate (0·12%), and more separates from the dimethyl ester on cooling. Its identity with the compound prepared from 1 : 2-7 : 8-diphthaloylcarbazole by dinitration, reduction, and benzoylation (G.P. 464,292) was confirmed. It was also identical with the product obtained by stirring 4 : 4'-dibenzamido-1 : 1'-dianthraquinonylamine (0·5 g.) with concentrated sulphuric acid at the room temperature for 7 hr. (0·45 g.) and crystallising from diethyl phthalate. The absorption of a solution in concentrated sulphuric acid exhibited max. at 268 (ε 3·91 × 10^4), 365 (ε 5·28 × 10^4), 380 (ε 5·28 × 10^4), 550—554 (ε 3·13 × 10^4), and 590 mμ (ε 4·02 × 10^4).

Hydrolysis.—The above derivative (0·97 g.) was heated with syrupy phosphoric acid (30 c.c.; *d* 1·75) at 180—190° for 7 hr. as described on p. 2313 (yield, 0·67 g.).

Deamination.—A solution of the diamine (0·65 g.) in concentrated sulphuric acid (20 c.c.) was diazotized by means of nitrosylsulphuric acid from sodium nitrite (0·2 g.) and concentrated sulphuric acid (10 c.c.). After addition to crushed ice the bisdiazonium salt separated as an almost insoluble precipitate. The suspension was reduced with hypophosphorous acid to a sandy solid which was washed until neutral and dried (0·6 g.). Sublimation *in vacuo* gave clusters of orange yellow needles of 1 : 2-7 : 8-diphthaloylcarbazole (Found : N, 3·5. Calc. for $C_{28}H_{13}O_4N$: N, 3·3%). A solution in concentrated sulphuric acid showed absorption max at 270 (ε 3·42 × 10^4) and 510 mμ (ε 1·97 × 10^4).

Hydrolysis of Acylaminoanthraquinones.—By the procedure described on p. 2312 the following results were obtained :

Compound	Weight (g.)	Temp.	Time (hr.)	Benzoic acid (g.) Found *	Benzoic acid (g.) Calc.
1-Amino-5-benzamidoanthraquinone †	0·913	170°	0·5	0·324	0·326
1-Benzamido-5-chloroanthraquinone	1·241	180	0·5	0·404	0·414
1-Amino-4-benzamidoanthraquinone	1·231	180	0·5	0·437	0·439
5 : 5'-Dibenzamido-1 : 1'-dianthraquinonylamine	0·562	180—200	1·5	0·121	0·205
	0·446	180—190	7·0	0·148	0·162

* Ether-extraction and sublimation.

† In this expt. the yield of 1 : 5-diaminoanthraquinone was 0·634 g. (calc. 0·635 g.).

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