

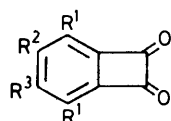
## Benzocyclobutenes. Part 6.<sup>1</sup> Reactions of Substituted Benzocyclobutene-1,2-diones with *o*-Phenylenediamine

By Omar Abou-Teim, Nigel P. Hacker, Robert B. Jansen, John F. W. McOmie,\* and David H. Perry, School of Chemistry, The University, Bristol BS8 1TS

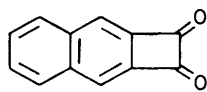
Condensation of the 4-hydroxy- (3), 4,5-dichloro- (4), 3,6-dimethoxy- (5), and 4,5-benzo- (9) derivatives of benzocyclobutene-1,2-dione with *o*-phenylenediamine gave the corresponding 5,10-diazabenzobiphenylenes (13)—(16) whereas the similar condensation of the 4-methoxy- (6), 4,5-dimethoxy- (7), and 4,5-dibromo- (8) derivatives, also cyclobuta[*l*]phenanthrene-1,2-dione, unexpectedly gave derivatives of dibenzo[*b,f*][1,4]-diazocine-6,11(5*H*,12*H*)-dione (20)—(23). Treatment of the 4-hydroxy-dione (3) with 1.4 equivalents of *o*-phenylenediamine gave 1,2-bis-(2-aminophenylimino)benzocyclobuten-4-ol (18) and condensation of the phenanthrodione with the diamine in presence of phosphoric anhydride gave dibenz[*a,c*]isoidolo[2,1-*a*]-benzimidazol-15-one (25).

CONDENSATION of benzocyclobutene-1,2-dione (BBD) (1) with *o*-phenylenediamine<sup>2</sup> and with substituted *o*-phenylenediamines<sup>3</sup> is known to give the corresponding 5,10-diazabenzobiphenylenes. So far only one derivative of BBD, namely the tetrachloro-derivative (2), has been condensed with *o*-phenylenediamine when the product was found to be the 2-arylquinoxalin-3-one (11).<sup>4</sup> We now describe the reaction of eight derivatives of BBD with *o*-phenylenediamine. Our results, together

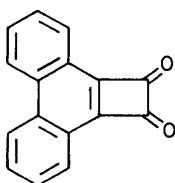
are exemplified by compounds (11), (13), (18), (20), and (25).



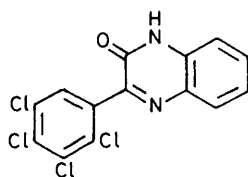
- (1)  $R^1 = R^2 = R^3 = H$   
 (2)  $R^1 = R^2 = R^3 = Cl$   
 (3)  $R^1 = R^3 = H, R^2 = OH$   
 (4)  $R^1 = H, R^2 = R^3 = Cl$   
 (5)  $R^1 = OMe, R^2 = R^3 = H$   
 (6)  $R^1 = R^3 = H, R^2 = OMe$   
 (7)  $R^1 = H, R^2 = R^3 = OMe$   
 (8)  $R^1 = H, R^2 = R^3 = Br$



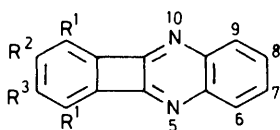
(9)



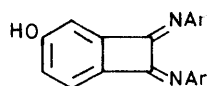
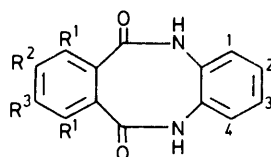
(10)



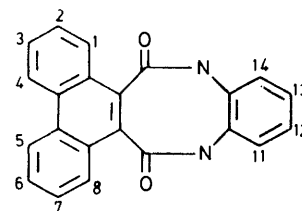
(11)



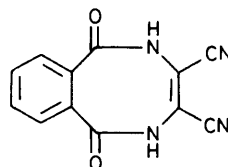
- (12)  $R^1 = R^2 = R^3 = H$   
 (13)  $R^1 = R^3 = H, R^2 = OH$   
 (14)  $R^1 = H, R^2 = R^3 = Cl$   
 (15)  $R^1 = OMe, R^2 = R^3 = H$   
 (16)  $R^1 = H, R^2 = R^3 = benzo$   
 (17)  $R^1 = R^3 = H, R^2 = OMe$

(18) Ar = *o*-aminophenyl

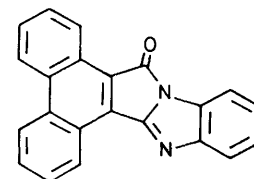
- (19)  $R^1 = R^2 = R^3 = H$   
 (20)  $R^1 = R^3 = H, R^2 = OMe$   
 (21)  $R^1 = H, R^2 = R^3 = OMe$   
 (22)  $R^1 = H, R^2 = R^3 = Br$



(23)



(24)



(25)

with the one mentioned above,<sup>4</sup> show that the reactions of *o*-phenylenediamine with derivatives of BBD can produce five different types of structure depending on the substituents and the reaction conditions. These types

Four derivatives of BBD, namely 4-hydroxy (3),<sup>1</sup> 4,5-dichloro (4),<sup>5</sup> 3,6-dimethoxy (5),<sup>1</sup> and 4,5-benzo (9),<sup>5</sup> reacted with a slight excess of *o*-phenylenediamine to give the corresponding diazabenzobiphenylenes (13)—(16) in 46, 66, 80, and 68% yields respectively. Methylation of the hydroxy-compound (13) with diazomethane gave the corresponding methoxy-derivative (17). When 4-hydroxy-BBD (3) was treated with 1.4 equivalents of the diamine it gave the bis-condensation product (18) in 33% yield. In contrast, the other four derivatives of BBD namely, 4-methoxy (6),<sup>1</sup> 4,5-dimethoxy (7),<sup>1</sup> and 4,5-dibromo (8),<sup>5</sup> also cyclobuta[*l*]phenanthrene-1,2-dione (10),<sup>6</sup> unexpectedly yielded derivatives of dibenzodiazocine, *viz.* compounds (20) (37%), (21) (84%), (22) (22%), and (23) (67%) respectively. The structure of these four diazocines was shown by analysis and by comparison of their spectroscopic properties with those of the parent compound (19), *e.g.* the dimethoxy-compound (21) had infrared bands at 3 205 and 1 640  $cm^{-1}$  (CO·NH) (the parent diazocine had  $\nu_{max}$  at 3 180 and 1 647  $cm^{-1}$ ), its n.m.r. spectrum in [<sup>2</sup>H<sub>6</sub>]dimethyl sulph-

oxide had a peak at  $\delta$  10.00 replaceable by D<sub>2</sub>O (the parent had a similarly replaceable peak at  $\delta$  10.06), and its mass spectrum showed a peak at  $M^+ - 18$  which was much stronger than the peak at  $M^+$  exactly as we had observed for the parent (19). The relevant spectroscopic properties of the diazocines (19), (20), (22), and (23) are recorded in the Experimental section.

The formation of dibenzodiazocines from derivatives of BBD represents the third method of synthesis of this ring system, the other two methods being the condensation of diethyl phthalate with *o*-phenylenediamine brought about by sodium hydride<sup>7</sup> and the oxidation of 5,10-diazabenzobiphenylene (12) with hydrogen peroxide in acetic acid.<sup>3</sup> The formation of dibenzodiazocines recorded in the present paper involves oxidation but we feel it is unlikely that the reaction proceeds *via* diazabenzobiphenylenes since we have previously shown that the parent compound (12) is not oxidised when air is bubbled through an ethanolic solution of it for 12 h.<sup>3</sup> The difference in behaviour between 4,5-dichloro- and 4,5-dibromo-BBD and between the two tetra-substituted derivatives (2) and (10) is particularly striking but at present we have no explanation for it, nor for the closely related reaction of BBD with diaminomaleonitrile which yields the benzodiazocine (24).<sup>8</sup>

In an attempt to synthesise the phenanthrene analogue of diazabenzobiphenylene, the phenanthrene dione (10) was heated with phosphoric anhydride in ethanol but the reaction gave the pyrrolidone (25). The same compound was formed when the phenanthrodiazocine (23) was sublimed *in vacuo* at ca. 200 °C. A similar transannular dehydration occurs with the parent diazocine (19).<sup>7</sup>

## EXPERIMENTAL

General directions are given in Part 4.<sup>5</sup> Great difficulty was experienced in getting satisfactory CHN analyses but the structures proposed are strongly supported by spectroscopic evidence.

*Condensation of 4-Hydroxybenzocyclobutene-1,2-dione with o-Phenylenediamine.*—(a) A mixture of the dione (3) (70 mg,  $4.73 \times 10^{-4}$  mol) and diamine (52 mg,  $4.81 \times 10^{-4}$  mol) in methanol (5 ml) and acetic acid (10 drops) was kept overnight. The product, 5,10-diazabenzobiphenylene-2-ol (13) (48 mg, 46%) separated as orange crystals which decomposed at ca. 290 °C (Found:  $M^+$  220.063. C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O requires  $M$  220.064,  $\nu_{\max}$  1 280, 1 260, and 750 cm<sup>-1</sup>,  $\lambda_{\max}$  237, 243, 272, 301sh, 370sh, 388, and 406 nm (log  $\epsilon$  4.14, 4.20, 4.41, 4.00, 3.94, 4.11, and 4.14).

(b) When the above experiment was repeated using the dione (3) (20 mg) and the diamine (20 mg) it gave 1,2-bis-(2-aminophenylimino)benzocyclobuten-4-ol (18) (10 mg, 33%) as needles which decomposed at ca. 270 °C (Found: C, 73.3; H, 5.1; N, 16.5. C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>O requires C, 73.1; H, 4.9; N, 17.1%),  $M^+$  328,  $\nu_{\max}$  3 300, 3 250, 1 600, 1 500, 1 300, 1 250, and 760 cm<sup>-1</sup>.

*2,3-Dichloro-5,10-diazabenzobiphenylene* (14).—A solution of the dione (4) (20 mg) and *o*-phenylenediamine (13 mg) in methanol (15 ml) and acetic acid (1 ml) gave, after a few hours, crystals of the biphenylene (14) (18 mg, 66%), m.p. 257–260 °C (Found:  $M^+$ , 271.991 2. C<sub>14</sub>H<sub>6</sub>N<sub>2</sub>Cl<sub>2</sub>

requires  $M$ , 271.990 8),  $\nu_{\max}$  1 308, 1 130, 903, and 763 cm<sup>-1</sup>.

*1,4-Dimethoxy-5,10-diazabenzobiphenylene* (15).—A solution of the dione (5) (20 mg) and *o*-phenylenediamine (12 mg) in methanol (5 ml) and acetic acid (0.5 ml) was warmed for 5 min then allowed to cool thereby giving compound (15) (22 mg, 80%), m.p. 228–230 °C (decomp.) (Found:  $M^+$  264.089 9. C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> requires  $M$ , 264.089 7),  $\nu_{\max}$  1 262, 1 104, 1 027, 823, 793, and 754 cm<sup>-1</sup>.

*5,12-Diazadibenzo[b,h]biphenylene* (16).—The dione (30 mg) and *o*-phenylenediamine (24 mg) in methanol (14 ml) and acetic acid (0.1 ml) was warmed for 5 min. On cooling the solution deposited the product (16) (32 mg, 68%) as yellow needles, m.p. 279–280 °C (from dimethyl sulphoxide) (Found: C, 84.5; H, 4.1. C<sub>18</sub>H<sub>10</sub>N<sub>2</sub> requires C, 85.0; H, 4.0%),  $M^+$  254,  $\nu_{\max}$  1 170, 1 112, 892, and 755 cm<sup>-1</sup>,  $\lambda_{\max}$  (MeCN) 217, 233, 243, 250, 278sh, 287, 305sh, 312, 342sh, 391, 404, and 416 nm (log  $\epsilon$  3.93, 3.98, 4.06, 4.06, 4.53, 4.63, 4.25, 4.29, 3.66, 4.11, 3.83, and 4.42). Dilute solutions of the compound show a bright bluish fluorescence in u.v. light and the u.v. spectrum is intermediate between those of dibenzobiphenylene<sup>9</sup> and 5,6,11,12-tetraazadibenzo[b,h]biphenylene.<sup>10</sup>

*Methylation of 2-Hydroxy-5,10-diazabiphenylene* (13).—An excess of diazomethane in ether was added to a solution of the hydroxy-compound (13) (33 mg) in ethanol (10 ml) and the mixture was kept at room temperature for 24 h. The solvent was removed by evaporation and the residue was sublimed at 125 °C and 0.03 mmHg thereby giving the methoxydiazabiphenylene (17) as yellow crystals (31 mg, 88%), m.p. 137–138 °C (Found: C, 77.5; H, 4.6; N, 12.0. C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O requires C, 77.0; H, 4.3; N, 12.0%),  $\nu_{\max}$  1 326, 1 275, 1 230, 825, and 765 cm<sup>-1</sup>,  $\delta$ (CDCl<sub>3</sub>) 6.7–7.7 (ArH, m) and 3.88 (OMe).

*8-Methoxydibenzo[b,f][1,4]diazocine-6,11(5H,12H)-dione* (20).—A mixture of the dione (6) (25 mg) and *o*-phenylenediamine (20 mg) in ethanol (10 ml) containing acetic acid (3 drops) was kept at room temperature for 24 h. The crystalline precipitate consisted of the diazocine (20) (16 mg, 37%), m.p. 238–240 °C (Found:  $M^+$ , 268.085. C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> requires  $M$ , 268.085),  $\nu_{\max}$  3 190, 3 025, and 1 647 cm<sup>-1</sup>,  $\delta$ ([<sup>2</sup>H<sub>6</sub>]DMSO) 9.95 and 10.09 (2NH, removed by D<sub>2</sub>O), 8.21 (H-10, d,  $J$  9 Hz), 6.91 (H-9, dd,  $J$  9 and 3 Hz), and 6.73 (H-7, d,  $J$  3 Hz),  $m/e$  268 (27%), 250 (100), 235 (31), 207 (28), and 179 (10).

*8,9-Dimethoxydibenzo[b,f][1,4]diazocine-6,11(5H,12H)-dione* (21).—A mixture of the dione (7) (30 mg) and *o*-phenylenediamine (20 mg) in methanol (10 ml) and acetic acid (1 ml) was warmed on a water-bath for 30 min then kept for 3 days at room temperature. The solid was recrystallised from aqueous dimethylformamide and gave the dimethoxydiazocine (21) (39 mg, 84%) as prisms, m.p. 248–250 °C (Found: C, 64.4; H, 5.0; N, 9.4. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub> requires C, 64.4; H, 4.7; N, 9.4%),  $\nu_{\max}$  3 205, 3 020, 1 640, 1 273, 1 222, 1 165 cm<sup>-1</sup>,  $\delta$ ([<sup>2</sup>H<sub>6</sub>]DMSO) 10.00 (2 NH, s, removed by D<sub>2</sub>O), 7.13 (4 ArH, m), 6.76 (2 ArH, s), and 3.70 (2 OMe, s),  $m/e$  298 (6%), 280 (40), 265 (8), 237 (17), 179 (71), and 178 (100).

*8,9-Dibromodibenzo[b,f][1,4]diazocine-6,11(5H,12H)-dione* (22).—A solution of the dione (8) (15 mg) and *o*-phenylenediamine (10 mg) in methanol (10 ml) and acetic acid (3 drops) gave, after 3 days at room temperature, the dibromodiazocine (22) as pale yellow prisms (4 mg, 22%), m.p. 254–255 °C (Found:  $m/e$ , 377.883. C<sub>14</sub>H<sub>6</sub><sup>81</sup>Br<sup>79</sup>BrN<sub>2</sub>O requires  $M - 18$ , 377.883),  $\nu_{\max}$  3 222, 3 095, 1 655, and 913 cm<sup>-1</sup>,  $\delta$ ([<sup>2</sup>H<sub>6</sub>]DMSO) 10.33br (2 NH, s), 7.63 (2 ArH, s),

and 7.16br (4 ArH, s), *m/e* 396 (0.2%), 378 (100), 300 (45), 298 (45), 218 (76), and 190 (43).

*Benzo*[b]*phenanthro*[9,10-*f*][1,4]*diazocine*-9,16(10H,15H)-*dione* (23).—A mixture of the dione (10) <sup>6</sup> (100 mg) and *o*-phenylenediamine (50 mg) in ethanol (15 ml) and acetic acid (1 ml) was boiled for 30 min then allowed to cool. The precipitate was recrystallised from ethanol and gave the *phenanthrodiazocine* (23) as yellow needles (100 mg, 67%), m.p. 330–335 °C (decomp) (Found: *M*<sup>+</sup>, 338.105. C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires *M*, 338.105), *v*<sub>max</sub>. 3 240, 3 080, 1 670, 1 610, 760, and 730 cm<sup>-1</sup>, *λ*<sub>max</sub>. (CH<sub>2</sub>Cl<sub>2</sub>) 256, 310, 353, 370, 387, 407, and 441 nm (log *ε* 4.25, 3.81, 3.42, 3.18, 3.21, 3.27, and 2.77), *m/e* 338 (1%), 320 (10), 304 (100), 277 (15), 228 (37), 201 (22), 176 (10), and 152 (16).

*Dibenz*[a,c]*isoindolo*[2,1-*a*]*benzimidazol*-15-*one* (25).—A mixture of the dione (10) (100 mg), *o*-phenylenediamine, and phosphoric anhydride (200 mg) in ethanol was boiled for 1 h. After cooling, the solid was collected and recrystallised from dimethyl sulphoxide to give the *pyrrolidone* (25) (98 mg, 71%) as orange needles which did not melt but sublimed at ca. 360 °C (Found: *M*<sup>+</sup>, 320.094. C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O requires *M*, 320.095), *v*<sub>max</sub>. 3 060, 1 770, 1 690, 1 610, 770, and 740 cm<sup>-1</sup>, *λ*<sub>max</sub>. (CH<sub>2</sub>Cl<sub>2</sub>) 251, 268, 274, 280, 307sh, 314, 322sh,

337, 353, 370, 387, 407 (log *ε* 4.49, 4.25, 4.22, 4.25, 4.32, 4.38, 4.33, 4.13, 4.05, 3.78, 3.92, and 3.99), *m/e* 320 (7%), 304 (100), 277 (12), 228 (19), 201 (9), 176 (4), and 152 (13).

*Dibenzo*[b,f][1,4]*diazocine*-6,11(5H,12H)-*dione* (19).—Compound (19) showed *m/e* 238 (16%), 220 (100), 194 (30), 192 (11), 164 (7), 102 (9), and 76 (16).

[0/1277 Received, 13th August, 1980]

#### REFERENCES

- <sup>1</sup> Part 5, O. Abou-Teim, R. B. Jansen, J. F. W. McOmie, and D. H. Perry, *J. Chem. Soc., Perkin Trans. I*, 1980, 1841.
- <sup>2</sup> M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Am. Chem. Soc.*, 1963, **85**, 2076.
- <sup>3</sup> J. W. Barton, M. C. Goodland, K. J. Gould, J. Hadley, and J. F. W. McOmie, *Tetrahedron*, 1978, **34**, 495.
- <sup>4</sup> A. Roedig, G. Bonse, E. M. Ganns, and H. Heinze, *Tetrahedron*, 1977, **33**, 2437.
- <sup>5</sup> Part 4, K. J. Gould, N. P. Hacker, J. F. W. McOmie, and D. H. Perry, *J. Chem. Soc., Perkin Trans. I*, 1980, 1834.
- <sup>6</sup> Part 7, N. P. Hacker and J. F. W. McOmie, in preparation.
- <sup>7</sup> W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, 1969, **34**, 2138.
- <sup>8</sup> J. W. Barton, M. C. Goodland, K. J. Gould, J. F. W. McOmie, W. R. Mound, and S. A. Saleh, *Tetrahedron*, 1979, **35**, 241.
- <sup>9</sup> R. F. Curtis and G. Viswanath, *J. Chem. Soc.*, 1959, 1670.
- <sup>10</sup> S. Hünig and H. Pütter, *Chem. Ber.*, 1977, **110**, 2532.