Persulphate Oxidations. Part XI.[1] Oxidative Dimerisation of Aminonaphthoquinones

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Persulphate oxidation of 2-amino-, 2-methylamino- and 2-ethylamino-1,4-naphthoquinone generated vinylogous π-amidyls which dimerised on carbon to form 3,3'-diamino-2,2'-binaphthoquinonyls; these may subsequently cyclise to dibenzocarbazolediquinones. Similar treatment of 2-dimethylamino-1,4-naphthoquinone gave a dinaphthofurandiquinone. Oxidation of 2-alkylamino-3-phenyl-1,4-naphthoquinones afforded benzocarbazolequinones; the 2-anilino- and 2-*o*-toluidino-analogues formed, in addition, *NN'*-dinaphthoquinonylbenzidines.

In previous papers in this series we have shown that a variety of products can be obtained by persulphate oxidation of carboxylic acids and amides. Vinylogous acids and amides are also potentially interesting substrates, and it has been noted[2] that simple 2-hydroxy-1,4-naphthoquinones (vinylogous acids) undergo oxidative dimerisation when treated with persulphate. We now extend this to the oxidation of aminonaphthoquinones.

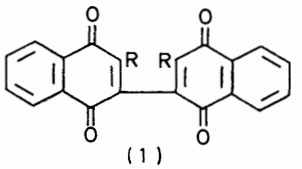
Persulphate oxidation of 2-amino-1,4-naphthoquinone gave the insoluble biquinone (1; R = NH_2) in good yield (see Table), the structure being confirmed by alkaline hydrolysis which afforded (1; R = OH) previously obtained by oxidation[2,3] of 2-hydroxy-1,4-naphthoquinone.

[1] Part X, A. R. Forrester, J. Skilling, and R. H. Thomson, *J.C.S. Perkin I*, 1974, 2161.

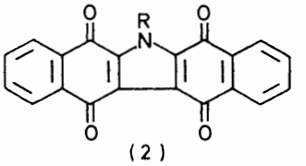
[2] K. Chandrasenan and R. H. Thomson, *Tetrahedron*, 1971, **27**, 2529.

[3] S. C. Hooker, *J. Amer. Chem. Soc.*, 1936, **58**, 1212.

Similarly 3-amino-5-methoxy-1,4-naphthoquinone gave the corresponding biquinone. However, oxidations of 2-methylamino- and 2-ethylamino-1,4-naphthoquinone



(1)



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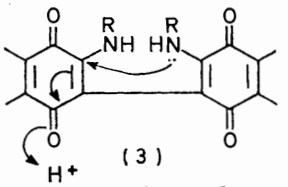

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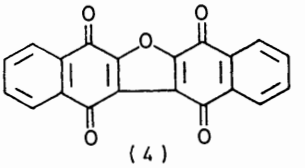
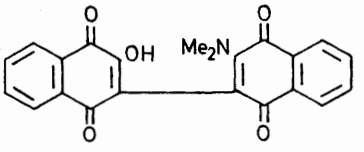


(4)

gave, as main products, the corresponding carbazolediquinones (2; R = Me or Et), together with smaller amounts of the purple-red dimers (1; R = NHMe or NHEt). The structures of these dimers were confirmed by synthesis from the parent biquinone (1; R = H) and the appropriate amine. The carbazolediquinones (2) were recognised by their yellow colour ($\lambda_{max.}$ *ca.* 256, 275, and 300 nm; *cf.* 2-acetylamino-1,4-naphthoquinone, $\lambda_{max.}$ 252, 285, and 337 nm), the absence of i.r. absorption above 3 000 cm^{-1}, their mass spectra, which showed successive losses of four molecules of carbon monoxide, and synthesis from the dimers (1; R = NHMe or NHEt). Conversion of the diamino-biquinones (1; R = NHMe or NHEt) into the carbazolediquinones (2) could be either an oxidative or a nucleophilic process but is evidently the latter (3) as (1; R = NHEt) could be converted into (2; R = Et) by heating in an aqueous solution made acidic by prior decomposition of persulphate. More

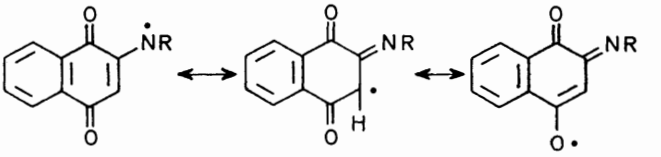


(1A)

conveniently the transformation (1) ⟶ (2) could be effected in boiling aqueous trifluoroacetic acid, although we were unable to cyclise (1; R = NH_2).

Clearly the diamino-biquinone (1; R = NMe_2) cannot cyclise in an exactly analogous fashion, and when 2-dimethylamino-1,4-naphthoquinone was oxidised the product, obtained in good yield, was the furodiquinone (4) (isomers [3] were not observed). Although (1; R = NM_2) was not detected this is a likely intermediate which suffers partial hydrolysis to give (1A) followed by intramolecular nucleophilic displacement of the dimethylamino- by the hydroxy-group. The possibility that (4) is formed by initial hydrolysis of the starting material followed by conversion into (1; R = OH) and dehydration, is ruled out because we confirmed [2] that (1; R = OH) does not give (4) under the reaction conditions.

The initial dimerisation step is of interest. We have shown [4a] that amidyls are generated by persulphate oxidation of amides, and the vinylogous amidyls derived from 2-amino-1,4-naphthoquinones can be represented by structure (5). Radical coupling at C-3 accounts for the formation of (1), and hence of (2). The only other possibility is that the central bond in (1) is formed by addition of a vinylogous amidyl (5) to an unoxidised quinone molecule. This seems unlikely because deliberate attempts to effect cross-coupling were unsuccessful. When equimolecular amounts of 2-ethylamino-1,4-naphthoquinone and 5-methoxy-1,4-naphthoquinone were oxidised with persulphate the



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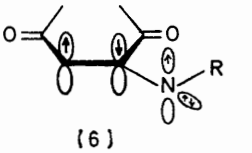

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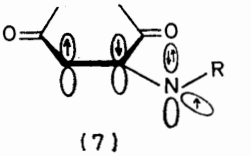


(7)

former was converted into (2; R = Et) (35%) whereas most (84%) of the methoxyquinone was unchanged. When the ethylaminoquinone was oxidised in the presence of 2 equiv. of 2-methoxy-1,4-naphthoquinone, again no unsymmetrical biquinone was formed.

Oxidation of 2-acetylamino-1,4-naphthoquinone did not lead to dimer formation, the product being 2-acetylamino-3-hydroxy-1,4-naphthoquinone formed by addition of a hydroxyl radical or sulphate radical-anion (followed by hydrolysis). This is consistent with the vinylogous imide structure of the acetylaminoquinone, imides being more resistant to oxidation than amides; [5] 35% of the starting quinone was recovered.

The electronic structure of amidyls (π- or δ-) has been the subject of considerable debate and experiment. There is e.s.r.[6] evidence and theoretical support [7] that they are π-radicals but the chemical evidence is less satisfactory. π-Radicals should react on oxygen as well as on nitrogen, but whereas reaction on nitrogen is well documented [8] reaction on oxygen has only been observed in two cases.[4a,b] The formation of diamino-

[4] (*a*) A. R. Forrester, A. S. Ingram, and R. H. Thomson, *J.C.S. Perkin I*, 1972, 2853; (*b*) B. Danieli, P. Manitto, and G. Russo, *Chem. Ind.*, 1969, 329; 1971, 203.

[5] E. Hedaya, R. L. Hinman, L. M. Kibler, and S. Theodoropolus, *J. Amer. Chem. Soc.*, 1964, **86**, 2727.

[6] W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, 1972, **94**, 6853; T. Koenig, J. A. Hoobler, and W. R. Mabey, *ibid.*, p. 2514.

[7] T. Koenig, J. A. Hoobler, C. E. Klopfenstein, G. Hedden, F. Sunderman, and B. R. Russell, *J. Amer. Chem. Soc.*, 1974, **96**, 4573.

[8] *E.g.* S. A. Glover, A. Goosen, and H. A. H. Lawe, *J.C.S. Perkin I*, 1973, 1647; D. Touchard and J. Lessard, *Tetrahedron Letters*, 1971, 4425; 1973, 3827; Y. L. Chow, J. N. S. Tam, C. J. Colón, and K. S. Pillay, *Canad. J. Chem.*, 1973, **51**, 2469.

biquinones (2; R = NHMe or NHEt) from 2-amino-1,4-naphthoquinones, and the absence of products formed by reaction on nitrogen, is clear evidence that the vinylogous amidyls are π-radicals, *i.e.* compound (5) should be represented as in (6) and not as in (7).

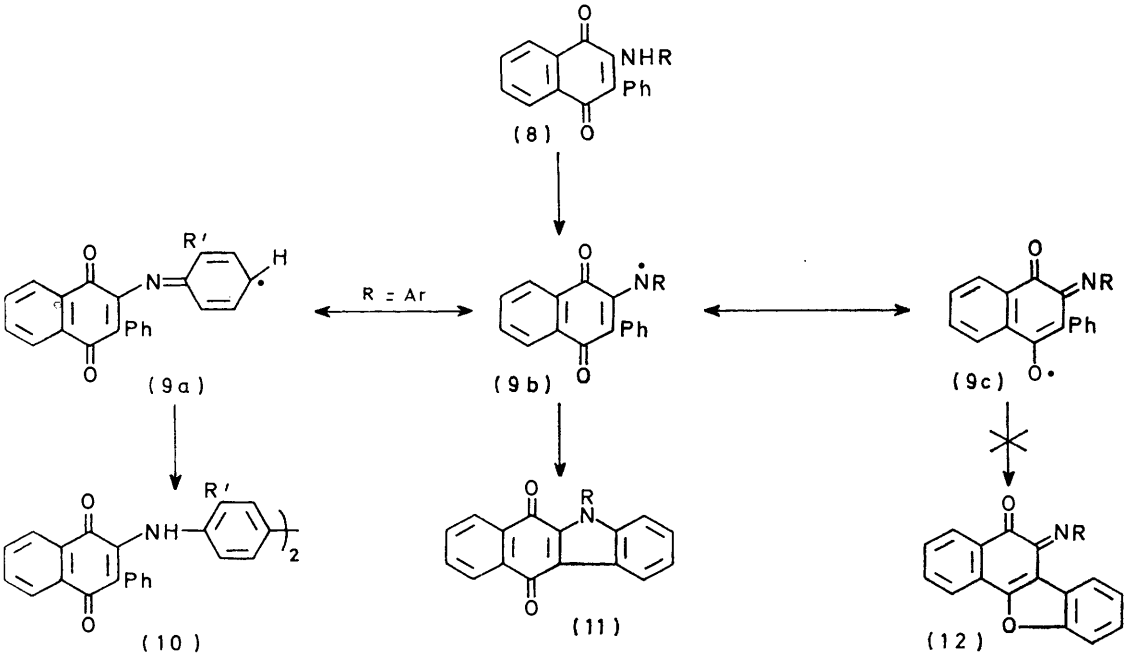
To encourage reaction on nitrogen and oxygen we also oxidised a series of 2-amino-3-phenyl-1,4-naphthoquinones (8). Very poor yields were obtained initially, owing to the low solubility of these quinones in water,

Products (%) from the oxidation of 2-amino-1,4-naphthoquinones with persulphate

1,4-Naphthoquinone	Biquinone (1)	Carbazole (2)	Carbazole (11)
2-NH_2	70		
2-MeNH	10	43	
2-EtNH	10	20 [a]	
2-Me_2N		74 [b]	
3-NH_2-5-MeO	47		
(8; R = H)			2
(8; R = Me)			17
(8; R = Bu^t)			9
(8; R = Ph)	26 [c]		22
(8; R = *o*-MeC_6H_4)	20 [c]		6
(8; R = *p*-MeC_6H_4)			32

[a] 42% in aqueous acetonitrile. [b] Furanodiquinone (4). [c] Biquinone (10).

but better results (Table) were achieved when the reactions were conducted in aqueous acetonitrile.[9] The compounds (8; R = Me, But, Ph, or *o*- or *p*-MeC_6H_4) afforded the corresponding carbazolequinones (11) but the parent (8; R = H) gave a complex mixture of compounds which did not include (11; R = H) (t.l.c.). This may be a consequence of further oxidation to which carbazoles are susceptible.[10] Interestingly the phenyl and *o*-tolyl analogues (8; R = Ph or *o*-MeC_6H_4) also gave modest amounts of the purple dimers (10; R = H or Me). These were generally similar to the monomers, and for (10; R′ = H) the structure was established by hydrolysis to give benzidine and 2-hydroxy-3-phenyl-1,4-naphthoquinone. These results show that the vinylogous amidyls generated by oxidation of the aminoquinones (8) can cyclise onto the adjacent phenyl group by way of the species (9b) to form (11), and the phenyl and *o*-tolyl analogues can, in addition, dimerise *via* the mesomeric form (9a) to produce (10). Cyclisation on oxygen (9c) to give furo-*o*-quinones [by hydrolysis of (12)] was not detected although a little of the furo-*p*-quinone (11; O in place of NR) was obtained by persulphate oxidation of 2-hydroxy-3-phenyl-1,4-naphthoquinone.



EXPERIMENTAL

T.l.c. refers to separations on silica gel plates in chloroform. Known compounds were identified by direct comparison (t.l.c., i.r., and m.p.) with authentic samples. Spectra were run in ethanol (u.v.), in Nujol (i.r.), and in $CDCl_3$ (n.m.r.) unless otherwise stated. Petrol refers to light petroleum, b.p. 40—60°.

Starting Materials.—2-Alkylaminonaphthoquinones were prepared by reaction of 2-methoxy-1,4-naphthoquinone with an excess of the appropriate amine, either neat or in ethanolic solution.

The following aminoquinones were prepared by heating 2-phenyl-1,4-naphthoquinone [11] under reflux with an excess of the appropriate amine in ethanol: 2-*amino*-3-*phenyl*-1,4-*naphthoquinone*, red needles, m.p. 178·5—179·5° (from ethanol) (Found: C, 76·8; H, 4·4; N, 5·7. $C_{16}H_{11}NO_2$ requires C, 77·1; H, 4·5; N, 5·6%), $\nu_{max.}$ 3420, 3300, and 1680 cm^{-1}, $\lambda_{max.}$ 273, 335, and 465 nm (log ε 4·38, 3·44, and 3·44), δ 8·18—7·38 (9H, m, ArH) and 5·20 (2H, s, NH_2); 2-*methylamino*-3-*phenyl*-1,4-*naphthoquinone*, red needles, m.p. 159—160° (from ethanol) (Found: C, 77·8; H, 5·2; N, 5·2.

[9] N. Jacobsen and K. Torssell, *Acta Chem. Scand.*, 1973, **27**, 3211.

[10] W. A. Waters and J. E. White, *J. Chem. Soc.* (*C*), 1968, 740.

[11] D. E. Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478.

$C_{17}H_{13}NO_2$ requires C, 77·6; H, 5·0; N, 5·2%), $\nu_{max.}$ 3280 and 1675 cm^{-1}, $\lambda_{max.}$ 279 and 458 nm (log ε 4·58 and 3·35), δ 8·20—7·30 (9H, m, ArH) and 2·40 (3H, d, *J* 6 Hz, NMe); 3-*phenyl*-2-*t*-*butylamino*-1,4-*naphthoquinone*, light red needles, m.p. 103—104° (from petrol) (Found: C, 78·6; H, 6·1; N, 4·8. $C_{20}H_{19}NO_2$ requires C, 78·7; H, 6·3; N, 4·6%), $\nu_{max.}$ 3280, 1680, and 1660 cm^{-1}, $\lambda_{max.}$ 278 and 430 nm (log ε 4·32 and 3·56),δ 8·10—7·30 (9H, m, ArH), and 1·10 (9H, s, Bu^t); also isolated from this reaction was a small quantity of 3,3′-*diphenyl*-2,2′-*bi*-1,4-*naphthoquinonyl*, yellow needles, m.p. 256—258° (from chloroform–petrol) (Found: M^+, 466·1206. $C_{32}H_{18}O_4$ requires *M*, 466·1205), $\nu_{max.}$ 1670 cm^{-1}, $\lambda_{max.}$ 252 and 320 nm (log ε 3·23 and 2·63), δ 8·26—6·68 (18H, m, ArH), *m/e* 468(7%), 467(13),466(32, M^+), 423(28), 422(100), 421(89), 405(7), 393(8), 379(10), 363(9), 361(20), 276(16),105(56), 104(35), 77(35), and 76(45); 2-*anilino*-3-*phenyl*-1,4-*naphthoquinone*, purple needles, m.p. 155—156° (from hexane) (Found: C, 81·3; H, 4·4; N, 4·6. $C_{22}H_{15}NO_2$ requires C, 81·2; H, 4·7; N, 4·3%), $\nu_{max.}$ 3280 and 1670 cm^{-1}, $\lambda_{max.}$ 285 and 500 nm (log ε 4·68 and 3·57), δ 8·17—6·45 (14H, m, ArH); 3-*phenyl*-2-(o-*tolylamino*)-1,4-*naphthoquinone*, purple needles, m.p. 106—108° (from hexane) (Found: C, 81·2; H, 5·1; N, 4·0 $C_{23}H_{17}NO_2$ requires C, 81·4; H, 5·1; N, 4·1%), $\nu_{max.}$ 3300 and 1670 cm^{-1}, $\lambda_{max.}$ 282 and 485 nm (log ε 4·39 and 3·57), δ 8·20—6·38 (13H, m, ArH) and 2·20 (3H, 2, ArMe); 3-*phenyl*-2-(p-*tolylamino*)-*naphthoquinone*, purple needles, m.p. 162—164° (from hexane) (Found: C, 81·2; H, 5·1; N, 4·2. $C_{23}H_{17}NO_2$ requires C, 81·4; H, 5·1; N, 4·1%), $\nu_{max.}$ 3340 and 1670 cm^{-1}, $\lambda_{max.}$ 283 and 494 nm (log ε 4·27 and 3·61), δ 8·22—6·44 (13H, m, ArH) and 2·14 (3H, s, ArMe).

3-*Amino*-5-*methoxy*-1,4-*naphthoquinone*.—To 5-methoxy-1,4-naphthoquinone (1 g) in acetic acid (15 ml) was added sodium azide (0·68 g) in water (2 ml) dropwise with stirring. After 2 days, water (2 ml) was added and the solution was neutralised (K_2CO_3) and extracted with chloroform. Evaporation of the dried extract, and chromatography of the residue on silica gel gave the *aminoquinone*,* red needles, m.p. 158—161° (from chloroform–petrol) (Found: C, 64·1; H, 4·4; N, 6·9%; M^+, 203·0582. $C_{11}H_9NO_3$ requires C, 65·0; H, 4·5; N, 6·6%; *M*, 203·0582), $\nu_{max.}$ 3440, 3260, and 1660 cm^{-1}, $\lambda_{max.}$ 260, 275sh, 390, and 440sh nm (log ε 4·09, 3·90, 257, and 2·47), δ 7·70—7·10 (3H, m, ArH), 5·82 (1H, s, quinone H), and 3·92 (3H, s, OMe). Hydrolysis with hot dilute sulphuric acid gave 3-hydroxy-5-methoxy-1,4-naphthoquinone, identical with authentic material and different from the 2-hydroxy-isomer.

Persulphate Oxidations.—To the quinone (0·002 mol) in water (200 ml) at 100° was added potassium persulphate (0·003 mol) in water (100 ml) dropwise, with stirring during 15 min. The mixture was stirred for a further 1 h at 100°. The solid was collected, dried, and extracted with chloroform (Soxhlet), and the filtrate was also extracted with chloroform and dried. The combined extracts were concentrated, and chromatographed on silica gel in chloroform.

Less soluble 2-amino-3-phenyl-1,4-naphthoquinones (0·001 mol) were dissolved in water (25 ml) and acetonitrile (25 ml) and oxidised at 80° by addition of potassium persulphate (0·002 mol) in water 25 ml) during 15 min. After 1 h the acetonitrile was removed by evaporation, and the aqueous residue worked up as above.

(*a*) 2-Amino-1,4-naphthoquinone gave 3,3′-*diamino* 2,2′-*bi*-1,4-*naphthoquinonyl* (1; R = NH_2) (70%), red needles, m.p. 320° (from ethanol) (Found: C, 70·0; H, 3·6; N, 8·4%; M^+, 344·0797. $C_{20}H_{12}N_2O_4$ requires C, 69·8; H, 3·5; N, 8·1%; *M*, 344·0792), $\nu_{max.}$ 3480—3320 and 1675 cm.$^{-1}$, $\lambda_{max.}$ 273, 335, and 465 nm (log ε 4·68, 3·84, and 3·78), δ [$(CD_3)_2SO$] 8·10–7·65 (8H, m, ArH) and 6·76 (4H, s, NH_2), *m/e* 345(14%), 344(85, M^+), 329(6), 328(32), 327(79), 316(18), 315(100), 300(5), 299(20), 287(7), 271(6), 239(6), 214(8), and 204(4). This quinone (250 mg) in ethanol (20 ml) was heated under reflux with 2M-sodium hydroxide (10 ml) for 2 h. The solvents were removed *in vacuo* leaving a dark red solid which was transferred, in acetone, to silica gel–5% oxalic acid plates. Elution with chloroform gave 3,3′-dihydroxy-2,2′-bi-1,4-naphthoquinonyl (1; R = OH) (60 mg, 25%).

(*b*) 3-Amino-5-methoxy-1,4-naphthoquinone afforded 3,3′-*diamino*-5,5′-*dimethoxy*-2,2′-*bi*-1,4-*naphthoquinonyl* (47%), red needles, m.p. 315° (decomp.) (from ethanol) (Found: C, 65·6; H, 3·6; N, 3·2%; M^+-1, 403·0926. $C_{22}H_{16}N_2O_6$ requires C, 65·4; H, 4·0; N, 3·2%; $M-1$, 403·0930),$\nu_{max.}$ 3400, 3220, and 1675 cm^{-1}, $\lambda_{max.}$ 266sh, 273, 285, and 410 nm (log ε 4·38, 4·45, 4·42, and 3·97), *m/e* 403(6%, $M-1$), 390(25), 389(100), 388(20), 387(63), 376(11), 375(14), 374(10), 373(8), 360(8), 359(27), 346(10), 345(8), 344(8), 343(7), 342(16), 340(11), 331(8), 330(13), 329(8), 328(8), 316(10), and 312(10).

(*c*) 2-Methylamino-1,4-naphthoquinone yielded 6-*methyldibenzo*[b,h]*carbazole*-5,13:7,12-*diquinone* (2; R = Me) (43%), yellow needles, m.p. 350° (from chloroform–petrol) (Found: C, 73·7; H, 3·0; N, 3·8%; M^+, 341·0686. $C_{21}H_{11}NO_4$ requires C, 73·9; H, 3·2; N, 4·1%; *M*, 341·0688), $\nu_{max.}$ 1690—1660 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 256, 275, and 300sh nm (log ε 4·44, 4·35, and 4·19), δ 8·35—7·64 (8H, m, ArH) and 4·68 (3H, s, NMe), *m/e* 343(5%), 342(19), 341(100, M^+), 340(23), 313(10), 312(25), 170·5(6), 105(7), 104(5), 85(23), 83(38), 77(8), and 76(9); and 3,3′-*bis*-*methylamino*-2,2′-*bi*-1,4-*naphthoquinonyl** (1; R = NHMe) (10%), red needles, m.p. 320° (from chloroform–petrol) (Found: N, 7·2%; M^+, 372·1109. $C_{22}H_{16}N_2O_4$ requires N, 7·5%; *M*, 372·1109), $\nu_{max.}$ 3260 and 1670 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 278 and 480 nm (log ε 4·60 and 3·51), δ 8·12—7·60 (8H, m, ArH) and 3·22 (6H, s, NMe), *m/e* 372(5%, M^+), 352(6), 344(5), 343(30), 342(90), 341(100), 340(32), 327(10), 313(20), 312(40), 285(11), 284(9), 256(11), 228(11), 227(14), 202(11), 201(13), and 200(12). The same compound was also prepared by adding ethanolic 33% methylamine (50 ml) to 2,2′-bi-1,4-naphthoquinonyl (2 g). After 1 h the solvent and excess of amine were removed by evaporation to yield the diamino-biquinone (1; R = NHMe) (68%), m.p. 320°.

This biquinone (100 mg) in trifluoroacetic acid (10 ml) and water (5 ml) was boiled under reflux for 15 min. On cooling, dibenzocarbazolediquinone (2; R = Me) separated (65%) identical with that prepared above.

(*d*) 2-Ethylamino-1,4-naphthoquinone gave 6-*ethyldibenzo*[b,h]*carbazole*-5,13 : 7,12-*diquinone* (2; R = Et) (20%),† yellow needles, m.p. 360° (from chloroform–petrol) (Found: C, 74·3; H, 3·9; N, 4·0%; M^+, 355·0841. $C_{22}H_{13}NO_4$ requires C, 74·4; H, 3·7; N, 3·9%; *M*, 355·0844), $\nu_{max.}$ 1685—1660 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 257, 275, and 300sh nm (log ε 4·58, 4·53, and 4·46), δ 8·37—7·66 (8H, m, ArH), 5·35 (2H, q, CH_2), and 1·58 (3H, t, CH_3), *m/e* 357(4%), 356(19), 355(94, M^+), 340(8), 328(18), 327(3), 311(9), 299(6), 214(6), 105(11), 87(8), 85(63), 77(22), and 76(10), and 3,3′-*bis*-*ethylamino*-2,2′-*bi*-1,4-*naphthoquinonyl* (1; R = NHEt) (10%), red needles, m.p. 360° (decomp.) (from chloroform–

* Satisfactory carbon and hydrogen analyses could not be achieved for this compound.

† Increased to 42% when the oxidation was carried out in aqueous acetonitrile.

petrol) (Found: C, 71·8; H, 5·3; N, 6·9%; M^+, 400·1422. $C_{24}H_{20}N_2O_4$ requires C, 72·0; H, 5·0; N, 7·0%; M, 400·1422), $\nu_{max.}$ (KBr) 3320 and 1670 cm^{-1}, $\lambda_{max.}$ 276 and 754 nm (log ε 4·53 and 3·62), δ 8·17—7·52 (8H, m, ArH), 6·0br (2H, s, 2NH), 3·30 (4H, q, $2CH_2$), and 1·17 (3H, t, $2CH_3$), *m/e* 400(6%, M^+), 357(22), 356(94), 355(10), 354(5), 341(6), 340(11), 329(8), 328(38), 327(22), 312(6), 311(13), 299(11), 204(5), and 105(14). This compound was also prepared by treating 2,2′-bi-1,4-naphthoquinonyl (100 mg) with 33% diethylamine solution in ethanol (15 ml). After 1 h solvent and excess of amine were removed, and the residue was chromatographed on silica in chloroform to give the diamino-biquinone (1; R = NHEt) (60%), m.p. 360° (decomp.), identical with that obtained above.

This biquinone (60 mg) in methanol (50 ml) was added to water (300 ml) in which potassium persulphate (8·1 g) had previously been decomposed by boiling for 1 h. After heating under reflux for 30 min the mixture was worked up in the usual way to give the dibenzocarbazolediquinone (2; R = Et) (29%) and starting material (32%).

(*e*) 2-Dimethylamino-1,4-naphthoquinone yielded dinaphtho[2,3-*b*:2′,3′-*d*]furan-5,13 : 7,12-diquinone (4) (74%), yellow needles, m.p. 350° (lit.,[3] 350°) (from chloroform–petrol), identical with an authentic sample (Found: M^+, 328·0369. Calc. for $C_{20}H_8O_5$: M, 328·0371).

(*f*) 2-Ethylamino-1,4-naphthoquinone (201 mg, 0·001 mol) and 5-methoxy-1,4-naphthoquinone (188 mg, 0·001 mol) in acetonitrile (25 ml) and water (25 ml) were oxidised with potassium persulphate (540 mg, 0·002 mol) in water (25 ml). Work up gave 6-ethyldibenzo[*b*,*h*]carbazole-5,13 : 7,12-diquinone (65 mg, 35%) and 5-methoxy-1,4-naphthoquinone (158 mg, 84%).

(*g*) 2-Ethylamino-1,4-naphthoquinone (201 mg, 0·001 mol) and 2-methoxy-1,4-naphthoquinone (376 mg, 0·002 mol) were oxidised with potassium persulphate (540 mg, 0·002 mol) in water (25 ml) to give 6-ethyldibenzo[*b*,*h*]carbazole-5,13 : 7,12-diquinone (15 mg, 9%), 2-ethylamino-1,4-naphthoquinone (50 mg, 25%), and 2-methoxy-1,4-naphthoquinone (223 mg, 60%).

(*h*) 2-Acetylamino-1,4-naphthoquinone afforded 2-acetylamino-3-hydroxy-1,4-naphthoquinone (16%), red needles, m.p. 224° (from ethanol) (lit.,[12] 219—220°), and starting material (12%). The same oxidation in aqueous acetonitrile gave the acetylamino-hydroxy-quinone (21%) and starting material (35%).

(*i*) 2-Methylamino-3-phenyl-1,4-naphthoquinone yielded *5-methylbenzo*[b]*carbazole-6,11-dione* (11; R = Me) (17%), yellow needles, m.p. 213—213·5° (from hexane) (Found: C, 78·3; H, 4·4; N, 5·3%; M^+, 261·0791. $C_{17}H_{11}NO_2$ requires C, 78·2; H, 4·2; N, 5·4%; M, 261·0789), $\nu_{max.}$ 1660 cm^{-1}, $\lambda_{max.}$ 280 and 385 nm (log ε 4·48 and 2·85), δ 8·30—7·16 (8H, m, ArH) and 4·04 (3H, s, NMe), *m/e* 262(16%), 261(100, M^+), 260(45), 247(3), 233(3), 232(16), 205(3), 204(14), 203(3), 177(3), and 175(5). This compound was also obtained from (11; R = H) by methylation with methyl iodide–acetone–potassium carbonate; it had m.p. 213—214°.

(*j*) 3-Phenyl-2-t-butylamino-1,4-naphthoquinone gave *5-t-butylbenzo*[b]*carbazole-6,11-dione* (11; R = Bu^t) (9%), yellow needles, m.p. 199—200° (from petrol) (Found: C, 78·9; H, 5·4; N, 4·8%; M^+, 303·1259. $C_{20}H_{17}NO_2$ requires C, 79·2; H, 5·6; N, 4·6%; M, 303·1259), $\nu_{max.}$ 1660 cm^{-1}, $\lambda_{max.}$ 261sh, 275, 283, and 385 nm (log ε 3·35, 3·57, 3·57, and 1·87), δ 8·68—7·38 (8H, m, ArH) and 2·00 (9H, s, Bu^t), *m/e* 303(3%, M^+), 248(18), 247(100), 219(14), 191(5), 190(11), 164(5), and 163(5).

(*k*) 2-Amino-3-phenyl-1,4-naphthoquinone gave a complex mixture of unidentified products. Oxidation in aqueous solution (without acetonitrile) also gave a complex mixture but it was possible to isolate *5H*-benzo[*b*]carbazole-6,11-dione (11; R = H) (2%), yellow needles, m.p. 306—308° (lit.,[13] 309—310°) (from petrol) and starting material (29%) was recovered.

(*l*) 2-Anilino-3-phenyl-1,4-naphthoquinone yielded *5-phenylbenzo*[b]*carbazole-6,11-dione* (11; R = Ph) (22%), yellow needles, m.p. 255—257° [from petrol (b.p. 80—100°)] (Found: C, 81·3; H, 4·3%; M^+, 323·0948. $C_{22}H_{13}NO_2$ requires C, 81·7; H, 4·1%; M, 323·0946), $\nu_{max.}$ 1670 and 1650 cm^{-1}, $\lambda_{max.}$ 260sh, 274, 282, and 382 nm (log ε 4·33, 4·40, 4·34, and 2·66), δ 8·20—6·76 (13H, m, ArH), *m/e* 324(18%), 323(100, M^+), 322(32), 294(6), 266(4), 265(5), 162(9), and 132(5), and NN′-*bis*-(*3-phenyl-1,4-naphthoquinon-2-yl*)*benzidine* * (10; R′ = H) (26%), purple needles, m.p. 268—270° (from chloroform–petrol) (Found: N, 4·4%; M^+, 648·2047. $C_{44}H_{28}N_2O_4$ requires N, 4·3%; M, 648·2048), $\nu_{max.}$ 3320, 1670, and 1640 cm^{-1}, $\lambda_{max.}$ 300 and 510 nm (log ε 4·65 and 3·21), δ 8·20—6·55 (26H, m, ArH), *m/e* 650(14%), 649(40), 648(100, M^+), 647(5), 416(5), 248(4), 222(8), 165(10), 105(5), 104(5), and 76(5). The quinone (20 mg) was hydrolysed by heating in ethanol (5 ml) with 2M-sodium hydroxide (2·5 ml) under reflux for 24 h. The ethanol was evaporated off, water (10 ml) was added, and the mixture was extracted with chloroform which was dried ($MgSO_4$) and evaporated to give benzidine (4 mg, 70%) identical with authentic material. The aqueous phase was acidified, and extracted with chloroform to give 2-hydroxy-3-phenyl-1,4-naphthoquinone (6 mg, 78%), identical with an authentic sample.

(*m*) 2-Phenyl-3-(*o*-tolylamino)-1,4-naphthoquinone afforded *5-o-tolylbenzo*[b]*carbazole-6,11-dione* * (11: R = *o*-MeC_6H_4) (60%), yellow needles, m.p. 210—212° (from petrol) (Found: M^+, 337·1103. $C_{23}H_{15}NO_2$ requires M, 337·1102), $\nu_{max.}$ (KBr) 1670 and 1660 cm^{-1}, δ 8·60—6·90 (12H, m, ArH) and 1·97 (3H, s, ArMe), *m/e* 338(19%), 337(100, M^+), 336(35), 322(5), 321(8), 320(35), 309(13), 308(28), 291(9), 278(8), 204(28), 168(10), 105(18), and 91(13), and NN′-*bis*-[3-(*o-tolyl*)-1,4-*naphthoquinon-2-yl*]*benzidine* * (10; R′ = Me) (20%), purple needles, m.p. 240—241° (from chloroform–petrol) (Found: M^+, 676·2361. $C_{46}H_{32}N_2O_4$ requires M, 676·2362), $\nu_{max.}$ 1670 cm^{-1}, δ 8·24—6·36 (24H, m, ArH) and 2·22 (6H, s, 2Me), *m/e* 678(22%), 677(45), 676(100, M^+), 675(5), 659(5), 248(5), 247(6), 176(14), 105(6), and 76(5).

(*o*) 2-Phenyl-3-(*p*-tolylamino)-1,4-naphthoquinone gave *5-p-tolylbenzo*[b]*carbazole-6,11-dione* (11; R = *p*-MeC_6H_4) (32%), yellow needles, m.p. 266—267° (from chloroform–petrol) (Found: C, 81·6; H, 4·5; N, 4·1%; M^+, 337·1100. $C_{23}H_{15}NO_2$ requires C, 81·9; H 4·5; N, 4·1%; M, 337·1102), $\nu_{max.}$ 1670 and 1650 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 260sh, 273, 285, and 388 nm (log ε 4·41, 4·47, 4·46, and 2·83), δ 8·56—7·10 (12H, m, ArH) and 2·49 (6H, s, 2Me), *m/e* 338(20%), 337(100, M^+), 336 (24), 323(5), 322(22), 308(6·5), 278(16), 168(8), 161(6), and 132(5).

(*p*) 2-Hydroxy-3-phenyl-1,4-naphthoquinone (0·465 g, 1·9m mol), after oxidation with persulphate (0·54 g, 2m mol) in water, gave benzo[*b*]naphtho[2,3-*d*]furan-6,11-dione (60 mg, 13%) as yellow needles, m.p. 243—244° (from petrol)

* Satisfactory carbon and hydrogen analyses could not be achieved for this compound.

[12] F. Kehrmann and O. Weichardt, *J. prakt. Chem.*, 1889, **40**, 179.
[13] K. Fries and F. Kerkow, *Annalen*, 1922, **427**, 281.
[14] J. N. Chatterjea, *J. Indian Chem. Soc.*, 1954, **31**, 101.

(lit.,[14] 245°), and starting material (54%). When the oxidation was repeated in acetonitrile–water using twice as much persulphate the above product was not formed.

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