Reactions between 2,5-Di-t-butyl-1,4-benzoquinone and Certain Primary Aliphatic Amines[1]

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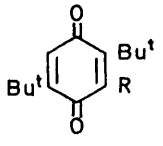
The title quinone reacts with n-propyl- and n-butyl-amine in the absence of air to give benzoxazoles and 3-amino-2,5-di-t-butyl-1,4-benzoquinone. In the presence of air, the formation of aminated quinone epoxides is observed to be a major reaction. No products were detected in the dark reaction of the title quinone with t-butylamine, but in the presence of light, aminated quinones containing a rearranged side-chain are obtained.

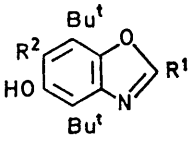
ALIPHATIC primary amines normally react with 1,4-benzoquinones to give nucleus-aminated quinones,[2] but other products may be formed. Carbazole-1,4-quinones have been reported to be among the products of the reactions of *p*-benzoquinone with n-butylamine[3] and ethyl glycinate.[4] We now report that benzoxazoles and quinone epoxides are formed in the reactions of the title quinone with n-propyl- and n-butyl-amine.

Reaction of 2,5-di-t-butyl-1,4-benzoquinone (Ia) with neat n-propylamine under nitrogen in the dark led to the isolation of three compounds, (Ib) (24%), (IIa) (14%), and (IIb) (5%). At the end of the reaction air was passed through the mixture in order to oxidise quinols to the quinone level. Much unchanged starting quinone was recovered.



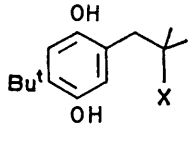
(I)

a; R = H
b; R = NH_2
c; R = $NHPr^n$



(II)

a; R^1 = Et, R^2 = H
b; R^1 = Et, R^2 = $NHPr^n$
c; R^1 = Pr^n, R^2 = H,
d; R^1 = Pr^n, R^2 = $NHBu^n$



(III)

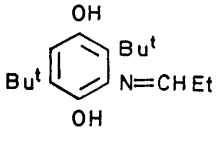
a; X = OEt
b; X = $NHPr^n$

The structure of the quinone (Ib) was deduced from analytical and spectral data and confirmed by synthesis from the quinone (Ia) and ethanolic ammonia. Moore and Wikholm[5] have recently described the synthesis of this quinone by reduction of the corresponding azido-quinone. A synthesis of the oxazole (IIa) from propionaldehyde and the hydroquinone of compound (Ib) confirmed its structure. The structure of the amino-benzoxazole (IIb) was deduced from spectroscopic evidence. In particular, its n.m.r. spectrum showed the absence of aromatic protons but contained signals assigned to two t-butyl groups in different environments and ethyl and n-propyl residues.

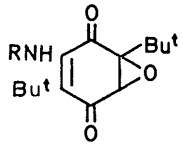
A similar reaction with n-butylamine in place of n-propylamine led to the isolation of the quinone (Ib) (28%) and the oxazoles (IIc) (13%) and (IId) (6%). The structures of the two oxazoles were deduced from spectral evidence and the former was synthesised from n-butyraldehyde and the hydroquinone of the quinone (Ib).

Photolysis of 2,5-di-t-butyl-1,4-benzoquinone in ethanol is known[6] to lead to the formation of quinol (IIIa) by rearrangement of the quinone side-chain. In an attempt to obtain the corresponding amino-quinol (IIIb), required in connection with other studies, we investigated the reaction of the quinone (Ia) with n-propylamine in sunlight, but only compounds (Ib), (IIa), and (IIb) were isolated. The yields of the oxazoles (IIa) and (IIb) were comparable to those of the dark reaction but rather less of the aminoquinonone (Ib) was isolated and in addition the amount of starting quinone recovered was smaller. Similar results were obtained from the reaction with n-butylamine in sunlight. The lower yield of the aminoquinone (Ib) may be explained by its removal by further reaction with the solvent. We have found that although a solution of the quinone (Ib) in benzene is stable in sunlight, a solution in neat n-propylamine is rapidly decolourised, yielding several unidentified polar products as evidenced by t.l.c.

The formation of compounds (Ib) and (IIa) may be explained by the intervention of the quinol (IV). Such a compound could arise by nuclear amination of the starting quinone and oxidation to give the quinone (Ic). Subsequent bond migration in the quinone imine tautomer would lead to the quinol (IV).[7] Intramolecular cyclisation and oxidation could give (IIa) and amine exchange (transalkylidenation) involving n-propylamine, followed by oxidation, the quinone (Ib).

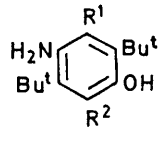


(IV)



(V)

a; R = Pr^n
b; R = Bu^n
c; R = H



(VI)

a; R^1 = OH, R^2 = H
b; R^1 = H, R^2 = OH

When the reaction of n-propylamine with quinone (Ia) was carried out in the dark in an open vessel, the yields of products (Ib), (IIa), and (IIb) were greatly reduced. The major product (20%) was assigned structure (Va)

[1] Preliminary communication, I. Baxter and W. R. Phillips, *Chem. Comm.*, 1972, 78.

[2] (*a*) D. W. Cameron and P. M. Scott, *J. Chem. Soc.*, 1964, 5569; (*b*) J. Kumanotani, F. Kagawa, A. Hikosaka, and K. Sugita, *Bull. Chem. Soc. Japan*, 1968, **41**, 2118; (*c*) A. Hikosaka, *ibid.*, 1970, **43**, 3928.

[3] K. Sugita and J. Kumanotani, *Bull. Chem. Soc. Japan*, 1964, **42**, 2043.

[4] P. A. Cranwell and R. D. Haworth, *Tetrahedron*, 1971, **27**, 1831.

[5] H. W. Moore and R. J. Wikholm, *Chem. Comm.*, 1971, 1073.

[6] C. M. Orlando, H. Mark, A. J. Bose, and M. S. Manhas, *J. Amer. Chem. Soc.*, 1967, **89**, 6527.

[7] *Cf.* E. J. Corey and K. Achiwa, *J. Amer. Chem. Soc.*, 1969, **91**, 1429.

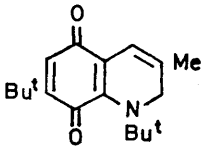
on the basis of spectral evidence. The presence of an NH and two carbonyl groups was indicated by the i.r. spectrum ($\nu_{max.}$ 3460, 1705, and 1650 cm^{-1}). The n.m.r. spectrum showed, in addition to signals assigned to two t-butyl groups and a propylamino-residue, a one-proton singlet (τ 6·40) attributable to the methine proton of an epoxide ring.[8] The epoxide (Vb) was obtained in an analogous manner. The related compound (Vc), required as a model, was prepared from the quinone (Ib) and alkaline hydrogen peroxide.[9]

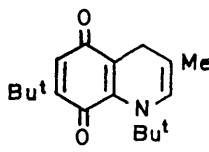
Attempts to obtain chemical evidence in support of structures (Va) and (Vb) by hydrolysis of the epoxide ring were unsatisfactory, the compounds being relatively stable under acid conditions and undergoing extensive reaction in alkali. The products from the latter reactions were not identified but mass spectrometry indicated that loss of the elements of carbon monoxide may have occurred. Such a loss could be achieved *via* a benzilic acid rearrangement of a hydroxy-quinone.[10] Catalytic reduction of the epoxide (Vc) gave, after aerial oxidation, the quinone (Ib) and an aromatic compound ($C_{14}H_{23}NO_2$). The i.r. spectrum of the latter showed the presence of amino- and hydroxy-groups but no carbonyl; its n.m.r. spectrum (in deuteriomethanol) contained only signals assigned to two t-butyl groups and one aromatic proton. Thus this product appears to be an amino-dihydroxy-di-t-butylbenzene. That it is not the hydroquinone derived from the quinone (Ib) was confirmed by comparison with authentic material. Therefore it seems likely, if no rearrangement has occurred, that it is either the resorcinol (VIa) or the catechol (VIb), products which could arise from the epoxide (Vc) by hydrogenolysis of the epoxide ring, reduction of a carbonyl group, and dehydration.

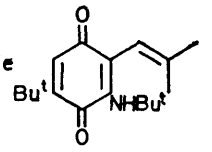
Catalytic reduction of the epoxide (Va) led to the formation of a colourless solution which turned red in air. However, the red product was unstable and t.l.c. of the resulting colourless solution showed the benzoxazole (IIa) to be among the reaction products. This suggests that hydrogenation partly converted the epoxide into 4-propylamino-2,5-di-t-butylhydroquinone which, after aerial oxidation to the quinone (Ic), rearranged as before to the benzoxazole. The accompanying reduction products, which could not be separated, appeared to be a mixture of alicyclic compounds containing carbonyl, hydroxy-, and propylamino-groups. In this connection, a hydroxycyclohexane-1,4-dione, together with other unidentified alicyclic compounds, has been isolated from the catalytic reduction of 2,3-epoxy-2,3-dihydro-2,5-di-t-butyl-1,4-benzoquinone.[11]

The formation of quinone epoxides from hydroquinones and oxygen in the presence of base has been described.[11]

When the quinone (Ia) was kept in neat t-butylamine in the dark for prolonged periods no significant reaction occurred, presumably because of steric hindrance. This failure was not unexpected in view of the observation[12] that t-butylamine reacts with *p*-benzoquinone only sluggishly. However, when a mixture of t-butylamine and the quinone (Ia) was kept in sunlight four products were isolated, albeit in low yields. One of these ($C_{18}H_{25}NO_2$) showed signals for two carbonyl groups in the i.r. spectrum ($\nu_{max.}$ 1660 and 1640 cm^{-1}) and this together with the u.v. spectrum ($\lambda_{max.}$ 287 and 550 nm) suggested that it might be an aminated 1,4-quinone. Its n.m.r. spectrum showed the presence of two different t-butyl groups and a quinonoid proton, together with signals assigned to a $-CH{=}CMe{-}CH_2-$ group. On the basis of this information formulae (VII) and (VIII) are suggested as possible structures for this quinone.

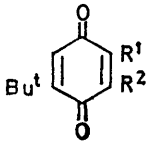

(VII)


(VIII)

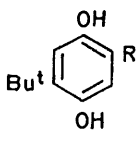

(IX)

Another product ($C_{18}H_{27}NO_2$) was also an aminated quinone, as evidenced by its i.r. spectrum ($\nu_{max.}$ 1670 and 1650 cm^{-1}) but in addition contained an NH group (3300 cm^{-1}). Its n.m.r. spectrum confirmed the presence of two t-butyl residues, a quinonoid proton, and a $CH{=}CMe_2$ group, and we have assigned structure (IX) to this quinone.

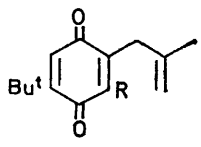
The other two products were identified as the isomeric quinones (Xa) and (Xb) by comparison with authentic samples obtained from the reaction of t-butylamine and t-butyl-1,4-benzoquinone.


(X)

a; R^1 = $NHBu^t$, R^2 = H
b; R^1 = H, R^2 = $NHBu^t$


(XI)

a; R = $CH{=}CMe_2$
b; R = $CH_2CMe{=}CH_2$


(XII)

a; R = $NHBu^n$
b; R = H
c; R = NH_2

The origin of the dealkylated quinones (Xa) and (Xb) is not known. That they arose from the presence of a small quantity of t-butyl-1,4-benzoquinone in the starting material is unlikely in view of the facts that (*a*) we were unable to detect the former in the latter by either t.l.c. or n.m.r. spectroscopy, although we showed these techniques to be capable of resolving such a mixture, and (*b*) quinones (Xa) and (Xb) were not produced in the corresponding dark reaction.

Since no amination could be detected in the dark reaction, it seems likely that the four products arise from photochemically derived products of the quinone (Ia).

[8] H. W. Moore, *J. Org. Chem.*, 1967, **32**, 1996.
[9] A. Rashid and G. Read, *J. Chem. Soc.* (*C*), 1967, 1323.
[10] U. Cuntze and H. Musso, *Chem. Ber.*, 1970, **103**, 62.
[11] F. R. Hewgill and S. L. Lee, *J. Chem. Soc.* (*C*), 1968, 1549.
[12] A. Hikosaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 3928.

The latter is known [13] to rearrange photochemically to give, among other products, the quinols (XIa) and (XIb), although the photochemical origin of (XIa) is not confirmed. If these two products are oxidised to the quinone level, at the expense of other quinoid species present, then amination may occur at the less sterically hindered nuclear position adjacent to the rearranged side-chain to give the quinones (IX) and (XIIa). The latter could undergo a base-catalysed cyclisation through its quinone imine tautomer to give ultimately the quinoline-quinone (VII) or (VIII). The quinones (Xa) and (Xb) could arise from photoproducts of 2,5-di-t-butyl-1,4-benzoquinone by the well documented dealkylation–amination process.[2a,14]

Some support for these suggestions comes from the observation that when the mixture of the quinones obtained by photolysis of the quinone (Ia) in benzene and subsequent oxidation with silver oxide was kept with t-butylamine in the dark then the quinoline (VII) or (VIII) and the quinone (Xb) were obtained in low yield.

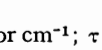
The reaction of the mixture of photoproducts obtained from the quinone (Ia), as described, with ethanolic ammonia was investigated in the hope that it would lead to the formation of another quinolinequinone, but we were able to isolate only the aminated quinone (XIIc).

EXPERIMENTAL

Unless otherwise stated i.r. spectra were measured for Nujol mulls. N.m.r. spectra were measured at 100 MHz with tetramethylsilane as internal reference. All integrations were consistent with the structural assignments. Light petroleum refers to the fraction boiling in the range 40—60°. T.l.c. was carried out on Kieselgel GF_{254}.

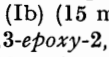
Reaction Between n-Propylamine and 2,5-*Di-t-butyl*-1,4-*benzoquinone*.—(*a*) The quinone (2·0 g) was dissolved in freshly distilled amine (200 ml) which had been degassed by passage of nitrogen for 30 min. The mixture was kept in a stoppered vessel for 1 month in the dark, then evaporated to dryness. The residue was dissolved in chloroform, and air passed through the solution for 1 h. The solution was evaporated to dryness and the residue chromatographed on SilicAR CC-7. Elution with carbon tetrachloride gave unchanged quinone (1·57 g). Elution with 15% dichloromethane–carbon tetrachloride gave a red fraction which was further purified by t.l.c. (light petroleum–acetone, 95 : 5) to give (i) 2-*ethyl*-6-*n-propylamino*-4,7-*di-t-butylbenzoxazol*-5-*ol* (IIb) (30 mg), m.p. 65—67° (95% EtOH) (Found: C, 72·1; H, 9·7; N, 8·7%; M^+, 332. $C_{20}H_{32}N_2O_2$ requires C, 72·3; H, 9·7; H, 8·4%; *M*, 332), $\nu_{max.}$ 3400, 1610, and 1565 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 240 and 300 nm (log ε 4·03 and 3·79), $\lambda_{infl.}$ 304 nm (log ε 3·78); τ ($CDCl_3$) 7·15 (q, *J* 7 Hz, CH_2·CH_3), 7·28 (t, *J* 7 Hz, N·CH_2·CH_2·CH_3), 8·24 (m, CH_2·CH_2·CH_3), 8·39 and 8·44 (2s, Bu^t), and 8·63 and 8·98 (2t, *J* 7 Hz, 2 × CH_2·CH_3); (ii) 3-*amino*-2,5-*di-t-butyl*-1,4-*benzoquinone* (Ib) (0·112 g), m.p. 109—110° (sublimed at 55° and 5 × 10^{-4} mmHg) (Found: C, 71·7; H, 9·2; N, 5·7. $C_{14}H_{21}NO_2$ requires C, 71·5; H, 9·0; N, 6·0%), $\lambda_{max.}$ ($CHCl_3$) 273 and 465 nm (log ε 4·13 and 3·21); $\nu_{max.}$ 3480, 3360, 1675, and 1645 cm^{-1}; τ (C_6D_6) 3·72 (s, C*H*=C), 5·30br (NH_2), and 8·69 and 8·95 (2s, Bu^t); (iii) 2-*ethyl*-4,7-*di-t-butylbenzoxazol*-5-*ol* (IIa) (0·075 g), m.p. 149—150° (from light petroleum) (Found: C, 74·2; H, 9·3; N, 5·0%; M^+, 275. $C_{17}H_{25}NO_2$ requires C, 74·2; H, 9·1; N, 5·1%; *M*, 275); $\lambda_{max.}$ (EtOH) 242 and 295 nm (log ε 4·00 and 3·61), $\nu_{max.}$ 3280, 1630w, 1590, and 1570 cm^{-1}; τ (C_6D_6) 3·71 (s, ArH), 5·49 (s, OH), 7·41 (q, *J* 7 Hz, CH_2·CH_3), 8·04 and 8·54 (2s, Bu^t), and 8·82 (t, *J* 7 Hz, CH_2·CH_3).

(*b*) Repetition of reaction (*a*) in sunlight gave unchanged quinone (1·22 g), oxazole (IIb) (65 mg), quinone (Ib) (63 mg), and oxazole (IIa) (0·157 g).

(*c*) Repetition of reaction (*a*) in an open vessel for 2 weeks gave oxazole (IIb) (5 mg), quinone (Ib) (41 mg), and oxazole (IIa) (20 mg). The major product was purified by t.l.c. (carbon tetrachloride) to give 2,3-*epoxy*-2,3-*dihydro*-6-*n-propylamino*-2,5-*di-t-butyl*-1,4-*benzoquinone* (Va) (0·53 g), b.p. 95—100° at 0·1 mmHg (Found: C, 69·8; H, 9·5; N, 4·7%; M^+, 293·1994. $C_{17}H_{27}NO_3$ requires C, 69·6; H, 9·3; N, 4·8%; *M*, 293·1990); $\lambda_{max.}$ (EtOH) 214, 280, and 377 nm (log ε 3·91, 3·67, and 3·65); $\nu_{max.}$ ($CHCl_3$) 3460, 1705, and 1650br cm^{-1}; τ ($CDCl_3$) 5·20br (s, NH), 6·40 (s, ), 6·85 (m, NH·CH_2·CH_2·CH_3), 8·46 (sextet, CH_2·CH_2·CH_3), 8·70 and 8·90 (2s, Bu^t), and 9·08 (t, *J* 7 Hz, CH_2·CH_2·CH_3).

Reaction between n-Butylamine and 2,5-*Di-t-butyl*-1,4-*benzoquinone*.—(*a*) The reaction was carried out with the quinone (2 g) and amine (200 ml) in the absence of air and light as already described. Chromatography led to the isolation of unchanged quinone (1·55 g), 3-amino-2,5-di-t-butyl-1,4-benzoquinone (0·165 g), 6-*n-butylamino*-2-*n-propyl*-4,7-*di-t-butylbenzoxazol*-5-*ol* (IId) (30 mg), m.p. 72—75° (from ethanol) (Found: C, 73·1; H, 9·9; N, 7·8%; M^+, 360. $C_{22}H_{36}N_2O_2$ requires C, 73·3; H, 10·1; N, 7·8%; *M*, 360); $\lambda_{max.}$ ($CHCl_3$) 250 and 300 nm (log ε 3·95 and 3·73), $\lambda_{infl.}$ 303·5 nm (log ε 3·73); $\nu_{max.}$ 3405, 1610, and 1560 cm^{-1}; τ ($CDCl_3$) 7·2 (m, CH_2·CH_2·CH_3 and N·CH_2·CH_2·CH_2·CH_3), 8·15 (m, CH_2·CH_2·CH_2), and 8·38 and 8·42 (2s, Bu^t) (the remainder of the spectrum was too complex to allow complete assignment), and 2-*n-propyl*-4,7-*di-t-butylbenzoxazol*-5-*ol* (IIc) (79 mg), m.p. 113—114° (from light petroleum) (Found: C, 74·9; H, 9·3; N, 5·1. $C_{18}H_{27}NO_2$ requires C, 74·7; H, 9·4; N, 4·8%); $\lambda_{max.}$ (EtOH) 244 and 295 nm (log ε 4·02 and 3·64); $\nu_{max.}$ 3180, 1630, 1590, and 1575 cm^{-1}; τ (C_6D_6) 3·82 (s, ArH), 5·68br (OH), 7·49 (t, *J* 7 Hz, CH_2·CH_2·CH_3), 8·17 and 8·64 (2s, Bu^t), 8·33 (m, CH_2·CH_2·CH_3), and 9·20 (t, *J* 7 Hz, CH_2·CH_2·CH_3).

(*b*) The reaction performed as in (*a*) but in sunlight gave unchanged starting material (1·45 g), oxazole (IId) (48 mg), quinone (Ib) (0·117 g), and oxazole (IIc) (0·103 g).

(*c*) The reaction was performed as in (*b*) with 1 g of quinone in an open vessel and gave oxazole (IId) (4 mg), quinone (Ib) (15 mg), oxazole (IIc) (13 mg), and 6-*n-butylamino*-2,3-*epoxy*-2,3-*dihydro*-2,5-*di-t-butyl*-1,4-*benzoquinone* (Vb) (230 mg), m.p. 67—68° (from ethanol) (Found: C, 70·4; H, 9·7; N, 4·3. $C_{18}H_{29}NO_3$ requires C, 70·3; H, 9·5; N, 4·6%); $\lambda_{max.}$ 215, 280, and 379 nm (log ε 4·08, 3·91, and 3·88); $\nu_{max.}$ 3400, 1708, and 1635 cm^{-1}; τ ($CDCl_3$) 5·30br (s, NH), 6·38 (s, ), 6·84 (m, N·CH_2·CH_2), 8·3—8·74 (m, CH_2·CH_2·CH_3), 8·67 and 8·87 (2s, Bu^t), and 9·07 (t, *J* 7 Hz, CH_2·CH_3).

3-*Amino*-2,5-*di-t-butyl*-1,4-*benzoquinone* (Ib).—Dry ammonia was bubbled through a solution of 2,5-di-t-butyl-1,4-benzoquinone (4 g) in absolute ethanol (400 ml) for 4 days in the absence of light. The solution was evaporated

[13] (*a*) S. Farid, *Chem. Comm.*, 1970, 303; (*b*) J. M Bruce and A. Chaudhry, *J.C.S. Perkin I*, 1972, 372.

[14] W. M. Horspool, P. I. Smith, and J. M. Tedder, *J.C.S. Perkin I*, 1972, 1024.

to dryness and the residue chromatographed on SilicAR CC-7. Elution with carbon tetrachloride gave unchanged starting material (3·0 g). Further elution, with dichloromethane–carbon tetrachloride (1 : 3), gave the quinone (0·93 g), m.p. and mixed m.p. 109—110°.

2-Ethyl-4,7-di-t-butylbenzoxazol-5-ol (IIa).—A solution of the foregoing quinone (0·30 g) in ether (20 ml) was shaken vigorously with a solution of sodium dithionite (4 g) in water (30 ml) until the red colour was discharged. The organic layer was evaporated to dryness; the residue was dissolved in glacial acetic acid (10 ml) and refluxed under nitrogen with propionaldehyde (0·23 g) for 4 h. The cooled mixture was neutralised with aqueous sodium hydrogen carbonate and extracted with chloroform. The dried extract ($MgSO_4$) was evaporated to dryness and the residue purified by t.l.c. (light petroleum–acetone, 9 : 1) to give the oxazole (0·105 g), m.p. and mixed m.p. 149—150° (from light petroleum).

2-n-Propyl-4,7-di-t-butylbenzoxazol-5-ol (IIc).—Prepared similarly from quinone (Ib) (0·150 g) and n-butyraldehyde (0·090 g), compound (IIc) had m.p. and mixed m.p. 113—114°.

Reaction of 2,5-Di-t-butyl-1,4-benzoquinone with t-Butylamine.—The quinone (2·0 g) was dissolved in the amine (200 ml) and kept in sunlight under nitrogen for 1 month. The mixture was worked up as before and the products purified by t.l.c. (light petroleum–acetone 95 : 5) to give 1,2(4?)-dihydro-3-methyl-1,7-di-t-butylquinoline-5,8-quinone (VII) or (VIII) (40 mg), m.p. 103—105° (Found: M^+, 287·1879. Calc. for $C_{18}H_{25}NO_2$: M, 287·1885); $\lambda_{max.}$ ($CHCl_3$) 287 and 550 nm; $\nu_{max.}$ 1660 and 1640 cm^{-1}; τ (C_6D_6) 3·50 (s, C*H*=CMe·CH_2), 3·59 (s, quinonoid CH), 6·67 and 8·52 (2s, CH=C*Me*·CH_2), and 8·87 and 8·94 (2s, Bu^t); *2-(2-methylprop-1-enyl)-5-t-butyl-3-t-butylamino-1,4-benzoquinone* (IX) (30 mg), b.p. 50—52° at $1·6 \times 10^{-4}$ mmHg (Found: C, 74·9; H, 9·2; N, 4·6%; M, 289. $C_{18}H_{27}NO_2$ requires C, 74·7; H, 9·4; N, 4·8%; M, 289); $\lambda_{max.}$ (EtOH) 229 and 512 nm (log ε 4·33 and 3·40); $\lambda_{infl.}$ 260 nm (log ε 4·10); $\nu_{max.}$ 3340, 1670, and 1650 cm^{-1}; τ ($CDCl_3$) 3·54 (s, quinonoid CH), 4·25 (s, olefinic CH), 6·28br (s, NH), 8·13 and 8·48 (2s, $C=CMe_2$), and 8·70 and 8·76 (2s, Bu^t); *2-t-butyl-6-t-butylamino-1,4-benzoquinone* (Xb) (30 mg), m.p. 108—109° (sublimed 60° at $1·6 \times 10^{-4}$ mmHg) (Found: C, 71·6; H, 9·0; N, 5·7. $C_{14}H_{21}NO_2$ requires C, 71·5; H, 9·0; N, 6·0%); $\lambda_{max.}$ (EtOH) 278 and 486 nm (log ε 4·24 and 3·47); $\nu_{max.}$ 3360, 1670, and 1635 cm^{-1}; τ ($CDCl_3$) 3·58 (d, J 2 Hz, 3-H), 4·26br (s, NH), 4·37 (d, J 2 Hz, 5-H), and 8·66 and 8·79 (2s, Bu^t); and *2-t-butyl-5-t-butylamino-1,4-benzoquinone* (Xa) (18 mg), m.p. 99—100° (sublimed 60° at $1·6 \times 10^{-4}$ mmHg) (Found: C, 71·8; H, 8·7; N, 5·8. $C_{14}H_{21}NO_2$ requires C, 71·5; H, 9·0; N, 6·0%); $\lambda_{max.}$ (EtOH) 275 and 480 nm (log ε 4·07 and 3·38); $\nu_{max.}$ 3370, 1675, and 1635 cm^{-1}; τ ($CDCl_3$) 3·57 (s, 3-H), 4·39 (s, 6-H), 4·52br (s, NH), and 8·64 and 8·72 (2s, Bu^t).

Reaction of 2-t-Butyl-1,4-benzoquinone with t-Butylamine.—A solution of the quinone (1·0 g) in freshly distilled amine (100 ml) was kept in the dark for 6 days and evaporated to dryness. Chromatography of the residue on SilicAR CC-7 (elution with 30% dichloromethane–carbon tetrachloride) gave 2-t-butyl-5-t-butylamino-1,4-benzoquinone (0·46 g), m.p. and mixed m.p. 99—100°. Further elution, with 50% dichloromethane–carbon tetrachloride, gave 2-t-butyl-6-t-butylamino-1,4-benzoquinone (0·25 g), m.p. and mixed m.p. 108—109°.

Reaction of 2-(2-Methylallyl)-5-t-butyl-1,4-benzoquinone (XIIb) *with t-Butylamine.*—A solution of 2,5-di-t-butyl-1,4-benzoquinone (4·0 g) in benzene (400 ml) was kept in sunlight under nitrogen for 1 week, and evaporated to dryness. The residue was dissolved in ether (150 ml) and heated under reflux with silver oxide (5 g) for 3 h. Filtration of this mixture followed by evaporation gave an oil (3·2 g), which was not purified further but was shown by n.m.r. to consist mainly of the title quinone (70%).

A solution of this mixture (2·0 g.) in degassed t-butylamine was kept in the dark for 1 month and evaporated to dryness. The residue was dissolved in chloroform and air was passed through the solution for 1 h. Concentration of this solution and t.l.c. (chloroform) gave a blue band which was further purified by t.l.c. (light petroleum–acetone, 95 : 5) to give the quinolinequinone (VII) or (VIII) and 2-t-butyl-6-t-butylamino-1,4-benzoquinone (5 mg), identical with material obtained earlier.

3-Amino-2-(2-methylallyl)-5-t-butyl-1,4-benzoquinone (XIIc).—The crude mixture of quinones obtained in the foregoing experiment (0·6 g) was dissolved in absolute ethanol (100 ml), treated with dry ammonia for 1 h, and kept for 48 h in the dark. Evaporation left a residue which was purified by t.l.c. (light petroleum–acetone, 9 : 1) and sublimation (55° at 5×10^{-4} mmHg) to afford the *aminoquinone* (80 mg), m.p. 103—104° (Found: C, 72·2; H, 8·4; N, 5·9. $C_{14}H_{19}NO_2$ requires C, 72·1; H, 8·2; N, 6·0%); $\lambda_{max.}$ (EtOH) 216, 274, and 494 nm (log ε 4·16, 3·89, and 3·66); $\nu_{max.}$ 3460, 3318, 1675, and 1635 cm^{-1}; τ ($CDCl_3$) 3·54 (s, quinonoid CH), 5·05br (NH_2), 5·20br (CH_2=CR_2), 6·85 (s, CH_2·C=C), 8·33 (CH_3–C=C), and 8·74 (s, Bu^t).

6-Amino-2,3-epoxy-2,3-dihydro-2,5-di-t-butyl-1,4-benzoquinone (Vc).—To a solution of 3-amino-2,5-di-t-butyl-1,4-benzoquinone (60 mg) in methanol (10 ml) was added a solution of alkaline hydrogen peroxide (1 ml) [prepared from 100 vol hydrogen peroxide (4 ml), water (5 ml), and sodium carbonate (1 g)]. The mixture was stirred at room temperature for 4 h and evaporated to dryness under reduced pressure. The residue was dissolved in chloroform and the solution dried ($MgSO_4$). Preparative t.l.c. (light petroleum–acetone, 9 : 1) gave the starting quinone (17 mg) and the *epoxide* (30 mg), m.p. 134—135° (from ethanol) (Found: C, 67·2; H, 8·2; N, 5·4. $C_{14}H_{21}NO_3$ requires C, 66·9; H, 8·4; N, 5·6%); $\nu_{max.}$ 3480, 3365 (NH_2), 1695, and 1640 cm^{-1} (C=O); $\lambda_{max.}$ (EtOH) 211, 254, and 372 nm (log ε 3·93, 3·71, and 3·70); τ ($CDCl_3$) 4·99br (s, NH_2), 6·32 (s, C*H*(O)C), and 8·66 and 8·87 (2s, Bu^t).

Catalytic Hydrogenation of the Epoxide (Vc).—A solution of the foregoing epoxide (0·110 g) in methanol (100 ml) was stirred under hydrogen with 5% palladium–charcoal (20 mg) for 4 h. The solution was filtered and air was passed through the filtrate for 30 min. The resulting red solution was evaporated to dryness and the residue dissolved in a small volume of hot chloroform. Addition of light petroleum and cooling gave a white solid which crystallised from chloroform–light petroleum to give either the resorcinol (VIa) or the catechol (VIb) (20 mg), m.p. 135—137° (Found: C, 70·5; H, 9·9; N, 6·2. Calc. for $C_{14}H_{23}NO_2$: C, 70·9; H, 9·8; N, 5·9%); $\nu_{max.}$ 3530, 3420, 3340, and 1635 cm^{-1}; $\lambda_{max.}$ 291 nm (log ε 3·85); τ (CD_3·OD) 3·13 (s, ArH) and 8·45 and 8·62 (2s, Bu^t).

Preparative t.l.c. of the mother liquors gave 3-amino-2,5-di-t-butyl-1,4-benzoquinone (10 mg), m.p. 107—109°.

Catalytic Hydrogenation of the Epoxide (Va).—A solution of the epoxide (0·106 g) in methanol (100 ml) was shaken

under hydrogen with 5% palladium–charcoal (20 mg) until the original yellow colour was discharged. The solution was filtered, aerated for 30 min, and evaporated to dryness. Attempted recrystallisation of the residue from chloroform–pentane gave an unidentified solid (37 mg), m.p. 140—142°, $\nu_{max.}$ 3340, 3200, 1720, and 1670 cm^{-1}; M^+ 297.

T.l.c. of the mother liquors showed the presence of the benzoxazole (IIa).

We thank the University of Ghana (Legon) for financial support to W. R. P.

[2/2169 *Received*, 18*th Spetember*, 1972]