2,3-Dihydro-1,4-Benzoxazine-6,7-Quinones and Related Compounds

By **I. Baxter** * and **R. B. Titman,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Treatment of suitably diaminated 1,4-benzoquinones (I) or monoaminated 2-hydroxy-1,4-benzoquinones (II) with sulphuric acid gives the title compounds. These exist predominantly in the *o*-hydroxy-*p*-quinone imine form rather than the *p*-amino-*o*-quinone form in chloroform solution, whereas in ethanol the tautomers are present in approximately equal amounts.

It has been reported that treatment of quinones (Ia) and (IIa) with concentrated sulphuric acid yields the benzoxazine (IIIa).[1] We have now investigated the scope of this reaction and examined the tautomerism of quinone (IIIa).

Oxazine (IIIa), a blue-black solid, displays a solvent-dependent electronic spectrum which may be explained in terms of the two tautomeric structures (IIIa) and (IVa). In ethanol (Figure 1), it forms a blue-purple solution ($\lambda_{max.}$ 302, 330s, and 560 nm.) similar to that of 4-dimethylamino-1,2-benzoquinone;[2] in chloroform (Figure 2) a yellow solution ($\lambda_{max.}$ 300 nm.) is obtained. (A concentrated solution in this solvent is red-brown.) We suggest that these absorptions correspond to a mixture (*ca.* 1 : 1) of tautomers (IIIa) and (IVa) in the case of the ethanolic solution and to almost pure tautomer (IVa) in chloroform. Evidence for these assignments was obtained by examination of the spectra of oxazines (IIIb) and (IVb), in which no tautomerism is possible. The black *N*-methyl compound (IIIb) showed maxima at 342 and 555 nm. in ethanol and at 341 and 535 nm. in chloroform, whereas the yellow *O*-methyl compound (IVb), obtained by the action of diazomethane on oxazine (IIIa), showed only a single maximum, at 289 nm. in ethanol and 292 nm. in chloroform. Moreover the extinction coefficients of the maxima of oxazine (IIIb) were approximately twice those of oxazine (IIIa) in ethanol. The oxazines (IIIc) and (IIId) showed similar tautomeric behaviour.

Treatment of the diaminoquinone (Ib) with sulphuric acid gave oxazine (IIIc) in good yield. The n.m.r. spectrum of the product showed the presence of two methyl groups in different environments attached to a quinonoid nucleus. The signals arising from the methylene and methine protons of the heterocyclic ring could not be assigned unequivocally, although one of the methylene protons gave a quartet centred at τ 6·45.

2-Aminobutanol reacted with *p*-xyloquinone to yield a tarry product from which the two diastereoisomeric bisaminated quinones (Ic) and the oxazine (IIId) were isolated. The oxazine was probably formed from quinones (Ic) during the isolation by chromatography. Both of the quinones (Ic) and the hydroxy-quinone (IIb)

[1] I. Baxter, D. W. Cameron, and R. G. F. Giles, *J. Chem. Soc.* (*C*), 1969, 1325.
[2] L. Horner and H. Lang, *Chem. Ber.*, 1956, **89**, 2768.

gave oxazine (IIId) on treatment with sulphuric acid. This oxazine crystallised from methanol as a dark blue solvate which slowly lost methanol under high vacuum to form the yellow unsolvated compound, presumably the quinone imine tautomer (IVc).

Oxazine (IIIe) was prepared from 2,5-bis-(*N*-methyl-2-hydroxyethylamino)-1,4-benzoquinone by the action

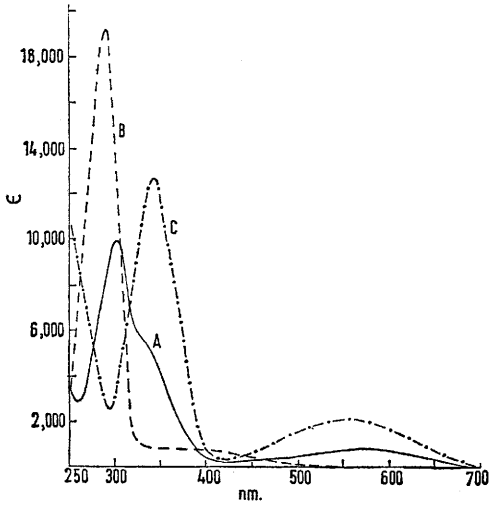


FIGURE 1 U.v. spectra for solutions in 95% ethanol: A, (IIIa); B, (IVb); C, (IIIb)

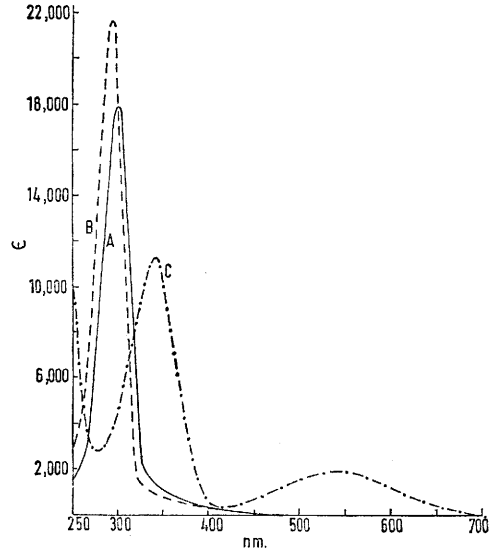
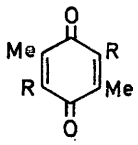


FIGURE 2 U.v. spectra for solutions in chloroform: A, (IIIa); B, (IVb); C, (IIIb)

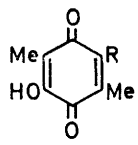
of sulphuric acid. This same oxazine was obtained, although in low yield, by the addition of 2-methylamino-ethanol to *o*-benzoquinone. This reaction was most successfully carried out by oxidising a mixture of catechol and 2-methylamino-ethanol in aqueous acetone with potassium iodate.[3]

It proved possible to prepare an *o*-quinone derived from the 1,5-benzoxazepine system by an extension of the acid-catalysed cyclisations already discussed. Treatment of the diamino-compound (Id) or, better, the



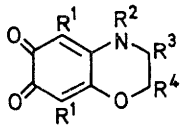
(I)

a; R = NH·CH_2·CH_2·OH
b; R = NH·CH_2·CHMe·OH
c; R = NH·CHEt·CH_2·OH
d; R = NH·$[CH_2]_3$·OH
e; R = N·CH_2·CH_2
f; R = N·$[CH_2]_2$·CH_2



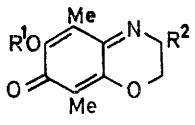
(II)

a; R = NH·CH_2·CH_2·OH
b; R = NH·CHEt·CH_2·OH
c; R = NH·$[CH_2]_3$·OH
d; R = N·$[CH_2]_2$·CH_2
e; R = NH·$[CH_2]_3$·O·$COCF_3$
f; R = H
g; R = NMe·CH_2·CH_2·OH

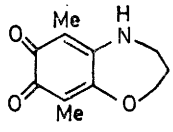


(III)

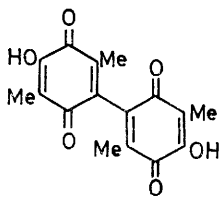
a; R^1 = Me, R^2 = R^3 = R^4 = H
b; R^1 = R^2 = Me, R^3 = R^4 = H
c; R^1 = R^4 = Me, R^2 = R^3 = H
d; R^1 = Me, R^2 = R^4 = H, R^3 = Et
e; R^1 = R^3 = R^4 = H, R^2 = Me



(IV)



(V)



(VI)

a; R^1 = R^2 = H
b; R^1 = Me, R^2 = H
c; R^1 = H, R^2 = Et

hydroxy-quinone (IIc) with sulphuric acid gave the quinone (V) in very low yield. The u.v. spectra of this compound in chloroform and ethanol showed that the concentration of the 4-amino-1,2-benzoquinone tautomer present was greater than that in the 1,4-benzoxazine series (see Experimental section). By analogy with the formation of oxazine (IIIa) from the aziridinyl-quinone (Ie) [1] it seemed possible that quinone (V) might be produced from the bisazetidinyl-quinone (If) by treatment with acid. However reaction with sulphuric acid failed to yield the benzoazepine but gave instead a low yield of the hydroxyazetidinyl-quinone (IId) as the sole isolated product.

Attempts to use organic acids, in place of sulphuric acid, as catalysts for the cyclisation reactions have, with one exception, proved unsuccessful. Treatment of quinone (Ia) with trifluoroacetic acid gave a mixture of oxazine (IIIa) and hydroxy-quinone (IIa), whereas under the same conditions quinone (Id) gave the ester (IIe) in quantitative yield. When 2,5-bis-(2-hydroxyethyl-amino)-1,4-benzoquinone was treated with trifluoroacetic

[3] *Cf.* H. W. Wanzlich, R. Gritzky, and H. Heidepriem, *Chem. Ber.*, 1963, **96**, 305.

acid for a short period 2,5-bis-(2-trifluoroacetoxyethylamino)-1,4-benzoquinone was the sole product. Toluene-*p*-sulphonic acid converted quinone (Id) into a mixture of quinone (IIc) and 3,6-dihydroxy-*p*-xyloquinone.

The diaminated quinones of type (I) were obtained by reaction of *p*-xyloquinone with a slight excess of the appropriate amine in ethanol. No diaminated quinone could be isolated from the reaction with 2-methylaminoethanol. Quinones (IIc) and (IId) were obtained from 3-hydroxy-2,5-dimethyl-1,4-benzoquinone (IIf) by treatment with the appropriate amine in ether as previously described for quinone (IIa).[1] Under the same conditions 2-aminobutanol and 2-methylaminoethanol caused only quantitative precipitation of the amine salt of quinone (IIf). Attack at the nucleus by these bulky amines will be sterically hindered to some extent; this may account for the lack of reaction, although relative solubilities of the amine salts of quinone (IIf) may also be important. When a ten-fold excess of 2-aminobutanol in a larger volume of ether was used the quinone (IIb) was formed in poor yield. The crude mixture of acidic quinones isolated was recycled to give a reasonable yield of quinone (IIb) together with a small quantity of the diquinone (VI). The formation of the latter by oxidation of the quinol derived from (IIf), under basic conditions has been described previously.[4] When the same amination procedure was applied to 2-methylaminoethanol, the reaction went to completion after one treatment, but under the mildly acidic conditions involved in the isolation the quinone (IIg) cyclised directly to oxazine (IIb).

The mechanism of the oxazine-forming reaction cannot be specified in detail but the first step may involve intramolecular attack by the alcoholic hydroxy-group at the carbon atom of the protonated carbonyl group to form a hemiacetal. Subsequent dehydration (and hydrolysis in the case of the diaminated quinones) would lead to the product. An alternative scheme which requires generation of a carbonium ion from the 2-hydroxyethylamino side-chain followed by electrophilic attack at the carbonyl oxygen atom seems unlikely in view of the fact that quinones (IIb) and (IIc) cyclise to give the expected products; the former in high yield. Rearrangement of the side-chains in these compounds under the influence of concentrated acid might be expected if carbonium ions were involved, *e.g.* quinone (IIc) would be expected to yield oxazine (IIIc) rather than compound (V). Indeed, as already mentioned, ready oxazine formation was observed in two cases under the catalytic influence of very mild acid, when carbonium ion formation would not be expected.

EXPERIMENTAL

Unless otherwise mentioned all u.v. spectra were measured for solutions in 95% ethanol. I.r. spectra were obtained for Nujol mulls. N.m.r. spectra were measured at 100 MHz for solutions in deuteriochloroform. All integrations were consistent with the assignments. T.l.c. was generally performed on Kieselgel HF 254, with 5% methanol in dichloromethane as developer.

2,3-Dihydro-4,5,8-trimethyl-1,4-benzoxazine-6,7-quinone (IIIb).—To a stirred solution of 2-methylaminoethanol (2 ml.) in ether (60 ml.) was added, during 30 min., a solution of 2-hydroxy-3,6-dimethyl-1,4-benzoquinone [5] (0·30 g.) in ether (30 ml.). The reaction was performed in the dark. After 1 hr. the ether was decanted, the residue was dissolved in water, and the solution was rendered slightly acidic. After 10 min. it was made slightly alkaline with ammonium hydroxide and extracted with dichloromethane. The extract, after chromatography, yielded the *quinone* (30 mg.), m.p. 133—135° (increases with rate of heating; value quoted obtained with the block pre-heated to 120°, heating rate 2°/min.) (Found: C, 64·0; H, 6·2; N, 6·5. $C_{11}H_{13}NO_3$ requires C, 63·7; H, 6·3; N, 6·8%); M^+ and $(M + 2)^+$ at *m/e* 207 and 209 (ratio 2 : 3), $\lambda_{max.}$ 236, 342, and 555 nm. (log ε 4·13, 4·10, and 3·11), $\lambda_{max.}$ (CHCl) 341, and 534 nm. (log ε 4·05 and 3·26), $\nu_{max.}$ 1655, 1630, and 1600 cm^{-1}, τ 5.69 and 6·47 (2t, *J* 5 Hz, N·CH_2·CH_2·O), 6·77 (s, NMe), and 8·10 and 8·20 (2s, C=CMe).

The ethereal supernatant liquid was evaporated to dryness and the residue, dissolved in cold concentrated sulphuric acid, was kept for 30 min., poured into water, and rendered just alkaline with aqueous ammonia. Extraction with dichloromethane followed by chromatography gave a further quantity of oxazine (10 mg.).

2,3-Dihydro-6-methoxy-5,8-dimethyl-1,4-benzoxazin-7-one (IVb).—To a solution of the oxazine (IIIa) [1] (0·10 g.) in chloroform (30 ml.) was added a solution of diazomethane (*ca.* 3 g.) in ether (150 ml.), and the mixture was kept for 7 hr. at −5 to 0°. Removal of the solvent followed by chromatography gave the *product* (75 mg.), m.p. 103° (decomp.) (from methanol) (Found: C, 64·0; H, 6·5; N, 6·7. $C_{11}H_{13}NO_3$ requires C, 63·7; H, 6·3; N, 6·8%), M^+ at *m/e* 207, $\lambda_{max.}$ 289 nm. (log ε 4·28), $\lambda_{max.}$ ($CHCl_3$) 292 nm. (log ε 4·33), $\nu_{max.}$ 1630 and 1605 $cm.^{-1}$, τ (60 MHz) 5·90—6·03 (m, N·CH_2·CH_2·O), 6·21 (s, OMe), and 8·03 and 8·25 (2s, C=CMe).

3,6-Bis-(2-hydroxypropylamino)-2,5-dimethyl-1,4-benzoquinone (Ib).—A mixture of *p*-xyloquinone (1·0 g.) and 1-aminopropan-2-ol (2·5 ml.) in ethanol (300 ml.) was kept in the dark for 2 weeks. Removal of the solvent, trituration of the resulting gum with methanol, and refrigeration yielded the *product* (0·36 g.), m.p. 159—160° (from methanol) (Found: C, 59·3; H, 7·8; N, 10·0. $C_{14}H_{22}N_2O_4$ requires C, 59·5; H, 7·9; N, 9·9%), M^+ at *m/e* 282, $\lambda_{max.}$ 224, 351, and 535 nm. (log ε 4·38, 4·40, and 2·90), $\nu_{max.}$ 3340, 3240, and 1630 $cm.^{-1}$, τ (CD_3·SO·CD_3) 2·90 (t, NH), 5·02 (d, OH), 6·08—6·63 (m, CH_2·CH), 8·03 (s, C=CMe), and 8·88 (d, *J* 6 Hz, CH·CH_3).

2,3-Dihydro-2,5,8-trimethyl-1,4-benzoxazine (IIIc).—A solution of the quinone (Ib) (0·10 g.) in concentrated sulphuric acid (3 ml.) was stirred at room temperature for 30 min., poured into water, rendered just alkaline with aqueous ammonia, and extracted with dichloromethane. The dried extract was evaporated to dryness and the residue was chromatographed on SilicAR CC-7. Elution with dichloromethane gave some minor, coloured by-products and subsequent elution with 3% ether in dichloro-

[4] H. Musso, U. v. Gizcki, U. I. Záhorszky, and D. Bormann, *Annalen*, 1964, **676**, 10.

[5] R. J. S. Beer, K. Clarke, H. F. Davenport, and A. Robertson, *J. Chem. Soc.*, 1951, 2029.

methane gave the *oxazine* (0·05 g.), m.p. 130—132° (from benzene) (increased with rate of heating; quoted value obtained with a block pre-heated to 120°, rate of heating 2°/min.) (Found: C, 63·8; H, 6·5; N, 6·6. $C_{11}H_{13}NO_3$ requires C, 63·7; H, 6·3; N, 6·8%), M^+ at *m/e* 207, $\lambda_{max.}$ 219, 302, and 565 nm. (log ε 4·20, 4·12, and 3·10), $\lambda_{max.}$ ($CHCl_3$) 300 nm. (log ε 4·42), $\nu_{max.}$ 3200br, 1650, and 1625 cm.$^{-1}$, τ 5·7—6·0 and 6·3—6·6 (2m, $CH_2{\cdot}CH{\cdot}CH_3$), 8·00 and 8·15 (2s, C=CMe), and 8·60 (d, *J* 6 Hz, $CH{\cdot}CH_3$).

Reaction of p-*Xyloquinone with* 2-*Aminobutanol*.—A solution of *p*-xyloquinone (2·0 g.) and 2-aminobutanol (3 ml.) in ethanol (600 ml.) was kept in the dark for 2 weeks, then evaporated to dryness under reduced pressure. A solution of the residue in dichloromethane was washed with M-hydrochloric acid and aqueous M-sodium hydroxide. Evaporation of the dried organic solution gave a gum which was purified by chromatography on SilicAR CC-7. Elution with dichloromethane containing ether (3%) gave a gum which was purified by further chromatography (Kieselgel HF 254). Crystallisation from methanol gave dark blue needles which, when kept in a vacuum, yielded the yellow *oxazine* (IVc) (35 mg.), m.p. 82—83° (Found: C, 65·3; H, 6·8; N, 6·2. $C_{12}H_{15}NO_3$ requires C, 65·2; H, 6·8; N, 6·3%), M^+ at *m/e* 221, $\lambda_{max.}$ 219, 302, and 565 nm. (log ε 4·18, 4·18, and 3·06), $\nu_{max.}$ 3375, 1625, and 1605 cm.$^{-1}$, τ 5·6—5·9 (m, CH), 6·0—6·3 (m, CH_2), 7·96 and 8·13 (2s, C=CMe), 8·1—8·5 (m, $CH_2{\cdot}CH_3$), and 8·88 (t, *J* 7 Hz, $CH_2{\cdot}CH_3$).

Further elution with ether–dichloromethane (1 : 1) gave *one diastereoisomer of quinone* (Ic) (65 mg.), m.p. 127·5—128° (from methanol) (Found: C, 61·9; H, 8·2; N, 8·8. $C_{16}H_{26}N_2O_4$ requires C, 61·9; H, 8·4; N, 9·0%), M^+ at *m/e* 310, $\lambda_{max.}$ 221, 351, and 535 nm. (log ε 4·42, 4·41, and 2·43), $\nu_{max.}$ (KBr) 3440, 3270, 1630w, and 1560s cm.$^{-1}$, τ ($CD_3{\cdot}SO{\cdot}CD_3$) 3·08 (d, *J* 10 Hz, NH), 5·07 (t, *J* 5 Hz, OH), 5·9—6·3br (N·CH), 6·53 (d, *J* 4 Hz, $CH_2{\cdot}OH$), 8·06 (s, C=CMe), 8·47 (quintet, *J* 7 Hz, $CH{\cdot}CH_2{\cdot}CH_3$), and 9·12 (t, *J* 7 Hz, $CH_2{\cdot}CH_3$).

Elution with ether gave the *second diastereoisomer of quinone* (Ic) (55 mg.), m.p. 116—116·5° (from methanol) (Found: C, 62·1; H, 8·7; N, 9·1. $C_{16}H_{26}N_2O_4$ requires C, 61·9; H, 8·4; N, 9·0%), M^+ at *m/e* 310, $\nu_{max.}$ (KBr) 3280, 3240, 1630w, and 1580s cm.$^{-1}$. This compound had u.v. and n.m.r. spectra identical with those of the other diastereoisomer.

2-*Hydroxy*-5-[1-(*hydroxymethyl*)*propyl*]*amino*-3,6-*dimethyl*-1,4-*benzoquinone* (IIb).—To a solution of 2-aminobutanol (1 ml.) in ether (30 ml.) was added a solution of 2-hydroxy-3,6-dimethyl-1,4-benzoquinone (0·15 g.) in ether (15 ml.) during 30 min., and the mixture was stirred in the dark. After 1 hr. the precipitate was filtered off and dissolved in water; the solution was acidified and extracted with dichloromethane. Evaporation of the extract gave a solid which contained a considerable amount of starting quinone and after dissolution in ether (15 ml.) this was treated with more amine and worked up as before. Chromatography of the dichloromethane extract on SilicAR CC-7 gave, on elution with dichloromethane, the starting quinone (25 mg.). Further elution gave 4,4′-dihydroxy-3,3′,6,6′-tetramethylbiphenyldiquinone (VI) (15 mg.), m.p. 207—210° (from benzene) (lit.,[4] 208—210°), τ 2·95br (exchangeable OH), and 8·06 and 8·12 (2s, C=CMe).

Elution with 0·5% methanol–dichloromethane gave the *quinone* (40 mg.), m.p. 101—103° (from benzene) (Found: C, 60·2; H, 7·1; N, 5·8. $C_{12}H_{17}NO_4$ requires C, 60·2; H, 7·2; N, 5·9%), M^+ at *m/e* 239, $\lambda_{max.}$ 314 and 527 nm. (log ε 4·25 and 3·14), $\nu_{max.}$ 3540, 3460, 3260, 1645, and 1605 cm.$^{-1}$, τ ($CD_3{\cdot}SO{\cdot}CD_3$) 3·50 (d, *J* 11 Hz, NH), 5·1br (OH), 6—7 (m, $N{\cdot}CH_2$, $CH_2{\cdot}OH$), 8·04 and 8·28 (2s, C=CMe), 8·2—8·6 (m, $CH{\cdot}CH_2{\cdot}CH_3$), and 9·11 (t, *J* 7 Hz, $CH_2{\cdot}CH_3$).

3-*Ethyl*-2,3-*dihydro*-5,8-*dimethyl*-1,4-*benzoxazine*-6,7-*quinone* (IIId, IVc).—(*a*) Quinone (IIb) (25 mg.) was dissolved in concentrated sulphuric acid (1 ml.). After 30 min. the solution was poured into water, rendered just alkaline with ammonium hydroxide, and extracted with dichloromethane. Evaporation of the dried extract gave a residue which after chromatography, crystallisation from methanol, and drying under high vacuum yielded the yellow oxazine (IVc) (15 mg.), m.p. 82—83°, i.r. spectrum identical with that of the material obtained before.

(*b*) The diastereoisomers of quinone (Ic) were each converted by treatment with sulphuric acid as in (*a*) into the oxazine (IVc) in approximately 60% yield.

2,3-*Dihydro*-4-*methyl*-1,4-*benzoxazine*-6,7-*quinone* (IIIe).—(*a*) 2,5-Bis-(*N*-methyl-2-hydroxyethylamino)-1,4-benzoquinone [6] (3·8 g.) was added slowly, with stirring, to concentrated sulphuric acid (100 ml.). When the addition was complete, the solution was stirred for 30 min., poured into ice–water, basified with ammonium hydroxide, and extracted with dichloromethane. The dried extract was concentrated and chromatographed on SilicAR CC-7. Elution with 1% methanol in dichloromethane gave various coloured minor products. Elution with 2% methanol gave the *quinone* (0·70 g.), m.p. 167—168° (decomp.) (increased with rate of heating; quoted value obtained with block pre-heated to 150°, rate of heating 2°/min.) (from methanol) (Found: C, 60·5; H, 5·1; N, 7·6. $C_9H_9NO_3$ requires C, 60·3; H, 5·1; N, 7·8%), *m/e* 181 $(M + 2)^+$ and 179 (M^+) (relative intensities *ca.* 3 : 1), $\lambda_{max.}$ 324 and 510 nm. (log ε 4·16 and 3·38), $\nu_{max.}$ 1650, 1630, and 1600 cm.$^{-1}$, τ ($CF_3{\cdot}CO_2H$) 3·36 and 3·70 (2s, C=C*H*), 5·38 and 5·76 (2t, *J* 5 Hz, $N{\cdot}CH_2{\cdot}CH_2{\cdot}O$), and 6·15 (s, NMe).

(*b*) To a stirred solution of catechol (1·1 g.) and 2-methylaminoethanol (0·75 g.) in a mixture of acetone (10 ml.) and water (10 ml.) was added a solution of potassium iodate (1·4 g.) in water (25 ml.). After 1 hr., the solution was diluted with water (100 ml.) and extracted with dichloromethane. The dried extract was concentrated and chromatographed, as in (*a*), to give the oxazine (IIIe) (15 mg.) (from methanol), identical with the material described in (*a*).

3,6-*Bis*-(3-*hydroxypropylamino*)-2,5-*dimethyl*-1,4-*benzoquinone* (Id).—A mixture of *p*-xyloquinone (0·20 g.) and 3-aminopropanol (0·5 ml.) in ethanol (60 ml.) was kept in the dark for 4 days. Evaporation followed by crystallisation from ethanol gave the *quinone* (0·13 g.), m.p. 151—152° (Found: C, 59·7; H, 7·8; N, 9·9. $C_{14}H_{22}N_2O_4$ requires C, 59·5; H, 7·9; N, 9·9%), M^+ at *m/e* 282, $\lambda_{max.}$ 221, 350, and 535 nm. (log ε 4·05, 4·17, and 2·46), $\nu_{max.}$ 3460, 3250, 1640, and 1630 cm.$^{-1}$, τ ($CD_3{\cdot}SO{\cdot}CD_3$) 2·86 (t, NH), 5·42 (t, OH), 6·45 (m, $O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N$), 8·04 (s, C=CMe) and 8·30 (quintet, *J* 6 Hz, $CH_2{\cdot}CH_2{\cdot}CH_2$).

2-*Hydroxy*-5-(3-*hydroxypropylamino*)-3,6-*dimethyl*-1,4-*benzoquinone* (IIc).—(*a*) To a solution of 3-aminopropanol (0·35 g.) in ether (30 ml.) was added a solution of 2-hydroxy-3,6-dimethyl-1,4-benzoquinone (0·30 g.) in ether (30 ml.). After 3 hr. the ether was decanted and the residue was dissolved in a small volume of water. Addition of dilute hydrochloric acid gave the *quinone* (0·16 g.), m.p. 150·5—

[6] K. H. König, *Chem. Ber.*, 1959, **92**, 257.

154° (from benzene) (Found: C, 58·9; H, 6·6; N, 6·4. $C_{11}H_{15}NO_4$ requires C, 58·6; H, 6·7; N, 6·2%), M^+ at *m/e* 225, $\lambda_{max.}$ 215, 314, and 530 nm. (log ε 4·39, 4·20, and 3·16), $\nu_{max.}$ 3560, 3450, 3260, 1645, and 1600 cm.$^{-1}$, τ (CD_3·SO·CD_3) 6·3—6·6 (m, CH_2·CH_2·CH_2), 8·01 and 8·29 (2s, C=CMe), and 8·14—8·4 (m, CH_2·CH_2·CH_2).

(*b*) A mixture of quinone (Id) (0·14 g.) and toluene-*p*-sulphonic acid (0·40 g.) in water (1 ml.) was stirred for 24 hr., diluted with water, and extracted with dichloromethane. Chromatography of the dried extract on SilicAR CC-7 gave, on elution with dichloromethane, 2,5-dihydroxy-3,6-dimethyl-1,4-benzoquinone (0·04 g.), m.p. and mixed m.p. 245° (from benzene). Further elution gave the quinone (IIc) (0·02 g.), identical with the material obtained from (*a*).

2,3,4,5-*Tetrahydro*-6,9-*dimethyl*-1,5-*benzoxazepine*-7,8-*quinone* (V).—The quinone (IIc) (1·0 g.) was added slowly, with stirring, to concentrated sulphuric acid (30 ml.). After 30 min., the solution was poured into ice–water, rendered just alkaline with aqueous ammonia, and extracted with dichloromethane. The dried extract was purified by t.l.c. The *oxazepine* (10 mg.) had m.p. 121—123° (pre-heated block at 115°; rate of heating 2°/min.) (from ethyl acetate) [Found: N, 6·9%; *M*, 207·090 (mass spectrum). $C_{11}H_{13}NO_3$ requires N, 6·8%; *M*, 207·090], $\lambda_{max.}$ 229, 326, and 560 nm. (log ε 4·45, 4·22, and 3·55), $\lambda_{max.}$ ($CHCl_3$) 308 and 520 (log ε 4·07 and 2·98), and *ca.* 340sh nm., $\nu_{max.}$ (KBr) 3280br, 1655, 1620w, 1610w, and 1600 cm.$^{-1}$, τ (CF_3·CO_2H) 5·59 and 5·76 (2t, overlapping, *J* 7 and 6 Hz, CH_2·CH_2·CH_2), 7·44 (quintet, CH_2·CH_2·CH_2), and 7·81 and 7·88 (2s, C=CMe).

5-*Azetidin*-1-*yl*-2-*hydroxy*-3,6-*dimethyl*-1,4-*benzoquinone* (IId).—(*a*) Prepared from azetidine (0·1 ml.) and 2-hydroxy-3,6-dimethyl-1,4-benzoquinone (0·10 g.) in ether as described for quinone (IIc), the *quinone* (0·08 g.) had m.p. 192—193° (from methanol) (Found: C, 63·6; H, 6·2; N, 7·0. $C_{11}H_{13}NO_3$ requires C, 63·7; H, 6·3; N, 6·8%), M^+ at *m/e* 207, $\lambda_{max.}$ 229, 322, and 547 nm. (log ε 4·25, 4·15, and 3·40), $\nu_{max.}$ 3255 and 1640 cm.$^{-1}$, τ 5·35 (t, *J* 8 Hz, CH_2·N), 7·63 (quintet, *J* 8 Hz, CH_2), and 8·00 and 8·21 (2s, C=CMe).

(*b*) A solution of 2,5-bisazetidin-1-yl-3,6-dimethyl-1,4-benzoquinone [7] (0·15 g.) in sulphuric acid (3 ml.) was kept at room temperature for 3 days, poured into water and extracted with dichloromethane. Chromatography of the dried extract gave the quinone (IId) (5 mg.), identical with the material obtained from (*a*).

Reactions of Various Quinones with Trifluoroacetic Acid.—(*a*) A solution of quinone (Ia) (0·20 g.) in trifluoroacetic acid (5 ml.) was kept overnight, poured into water, neutralised to pH 7, and extracted with dichloromethane. Chromatography on SilicAR CC-7 and elution with dichloromethane gave oxazine (IIIa) (35 mg.) (from benzene), identical with an authentic sample.[1]

Acidification of the aqueous solution to pH 4 followed by extraction with dichloromethane gave quinone (IIa) (25 mg.) (from benzene), identical with an authentic sample.[1]

(*b*) A solution of quinone (Id) (0·20 g.) in trifluoroacetic acid (5 ml.) was kept overnight and evaporated to dryness to give 2-*hydroxy*-5-(3-*trifluoroacetoxypropylamino*)-3 6-*dimethyl*-1 4-*benzoquinone* (IIe) in quantitative yield, m.p. 150—152° (from benzene) (Found: C 48·7; H 4·5; N 4·1. $C_{13}H_{14}F_3NO_5$ requires C, 48·7; H, 4·4; N, 4·4%), M^+ at *m/e* 321 $\lambda_{max.}$ 213, 313, and 525 nm. (log ε 4·30, 4·23, and 3·15), $\nu_{max.}$ 3280, 1795, 1650, and 1610 cm.$^{-1}$ τ 5·48, (t, *J* 6 Hz, CH_2), 6·22 (t, *J* 7 Hz, CH_2), 7·85 and 8·06 (2s, C=Me), and 7·82 (quintet, *J* 6 Hz, CH_2·CH_2·CH_2).

(*c*) 2,5-Bis-(2-hydroxyethylamino)-1,4-benzoquinone [6] (0·20 g.) was dissolved in trifluoroacetic acid (3 ml.); the solution was kept at room temperature for 30 min., then evaporated to dryness. Recrystallisation from methanol gave 2,5-*bis*-(2-*trifluoroacetoxyethylamino*)-1,4-*benzoquinone* (0·04 g.), m.p. 179° (Found: C, 40·4; H, 3·1; N, 6·4. $C_{14}H_{12}F_6N_2O_6$ requires C, 40·2; H, 2·9; N, 6·7%), $\lambda_{max.}$ 3320, 1760, 1640, and 1600 cm.$^{-1}$. Concentration of the mother liquors gave unchanged starting material (0·12 g.).

We thank the S.R.C. for a studentship (to R. B. T.).

[0/397 *Received*, *March* 13*th*, 1970]

[7] D. W. Cameron and R. G. F. Giles, *J. Chem. Soc.* (*C*), 1968, 1461.