The Reaction of 2,5-Di-t-butyl-1,4-benzoquinone with n-Propylamine

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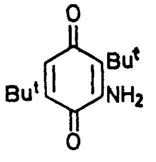
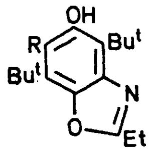
Summary Compounds (I), (IIa), and (IIb) have been isolated from the reaction of the title quinone and neat n-propylamine in the absence of air, while the epoxide (III) is a significant product when the reaction is carried out in air.

The reaction of aliphatic primary amines with 1,4-benzoquinones to give nuclear aminated quinones is well known.[1] Other products may be formed, *e.g.* carbazole quinones from the reactions of benzoquinone with n-butylamine[2] and ethyl glycinate.[1d] We have now found that treatment of

2,5-di-t-butyl-1,4-benzoquinone with neat n-propylamine under nitrogen at room temperature for prolonged periods in the dark does not lead to the isolation of the expected aminated quinone but instead yields several products among which we have identified compounds (I), (IIa), and (IIb). At the end of the reaction air was passed through the mixture in order to oxidise any quinols to the quinone level. A large quantity of unreacted starting quinone was recovered. The structure of quinone (I)† (24%) m.p. 109—110° was confirmed by synthesis from 2,5-di-t-butyl-1,4-benzoquinone and ethanolic ammonia. The preparation of this compound by an alternative route has been described recently.[3] The oxazole (IIa)† (14%) m.p. 149—150° was synthesised from the hydroquinone derived from compound (I) and propionaldehyde. The aminated oxazole (IIb)† (5%) had m.p. 65—67°.

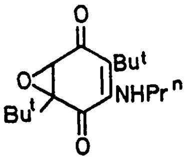


(I)

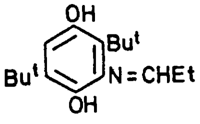


(II)

a; R = H
b; R = NHPr^n



(III)



(IV)

The formation of compounds (I) and (IIa) may be explained by the intervention of the quinol (IV).[4] Intramolecular cyclisation and oxidation yields (IIa) and transalkylidenation involving n-propylamine followed by oxidation, quinone (I).

When the reaction was repeated in the presence of air, a new product (in addition to those mentioned above) was isolated (20%) and assigned structure (III) on the basis of its spectral properties [b.p. 95—100°/0·1 mm; M^+ at m/e 293·1994; $C_{17}H_{27}NO_3$ requires 293·1990; ν_{max} ($CHCl_3$) 3460, 1715, and 1660 (br); λ_{max} (EtOH) 280 and 377 nm (log ϵ3·67 and 3·65); τ ($CDCl_3$) 5·20 (1H, br. s, NH), 6·40 (1H, s, O-CH), 6·85 (2H, m, NHCH_2CH$_2$CH$_3$), 8·46 (2H, sextet, CH$_2$CH_2CH$_3$), 8·70 and 8·90 (18H, 2s, Bu^t), and 9·08 (3H, t, J 7 Hz, CH$_2$CH$_2$CH_3)]. The formation of quinone epoxides from hydroquinones and oxygen in the presence of base has been reported.[5]

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† These compounds gave satisfactory elemental analysis and mass spectra. Other spectroscopic properties (n.m.r., i.r., and u.v.–visible) were consistent with the structures shown.

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