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The Formation of 3-*n*-Butylamino-7-hydroxy-9-*n*-butyl-carbazolquinone(1,4) in the Reaction of *p*-Benzoquinone with *n*-Butylamine

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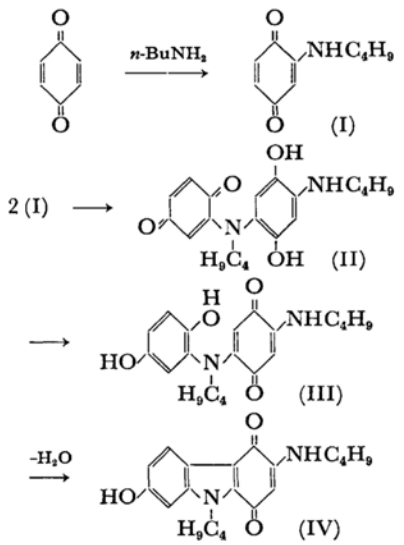
The reaction of *p*-benzoquinone with amines has been employed conveniently as a method of preparing 2,5-diamino-*p*-benzoquinoid compounds;[1] however, the details of the reaction remain to be elucidated. For instance, it is found in our laboratory that the reactions generally yield considerable amounts of resinous matter, especially with aliphatic amines.

We will report that, in the reaction of *p*-benzoquinone with alcoholic *n*-butylamine, a new compound, 3-*n*-butylamino-7-hydroxy-9-*n*-butyl-carbazolquinone(1,4) (IV), is formed in appropriate quantity, together with 2,5-bis(*n*-butylamino)-*p*-benzoquinone. The following scheme may be proposed for the formation of the carbazolquinone. I is formed through two steps:[1] (a) the nucleophilic 1,4-addition of the amine to the quinone to give an amino-quinol, and (b) the oxidation of the quinol with *p*-benzoquinone. III is obtained from I *via* a route similar to that described for I: the formation of III through II is due to the reductive potential of the diaminoquinone nucleus being more negative than that of the monoaminoquinone nucleus.



The compound (IV) was separated fractionally by recrystallization, and its molecular weight and formula were determined by the VPO method and by elementary analysis respectively. The structure of IV was confirmed as follows. The polarographic potential, −0.48 V (*vs.* SCE), measured at 25°C in a mixed solvent (1 : 1 v/v) of isopropanol and a phosphate buffer (pH, 6.0), indicates that IV has a diamino-*p*-benzoquinone nucleus.[2] This is supported by the following UV and IR spectral data: $\lambda_{max}^{CHCl_3}$ 354 mμ (ε, 17000), attributable to the π–π* transition band of the quinone nucleus; 3370 (m. ν_{N-H}), 1650 (m. $\nu_{C=C}$), 1590 (s. $\nu_{C=O}$), and 1510 cm^{-1} (s. amido II type band).[2] The intensity of the ν_{N-H} band of IV was found IR spectroscopically to be equivalent to one N–H group per mole unlike that of 2,5-bis(*n*-butylamino)-*p*-benzoquinone. The NMR spectrum in pyridine showed signals at 8.9—9.4 (triplet, 6H, $-CH_2-C\underline{H}_3$), 8.0—9.0 (multiplet, 8H, $>N-CH_2-C\underline{H}_2-C\underline{H}_2-CH_3$), 6.6—7.1 (quartet, 2H, $-NH-C\underline{H}_2-$), and 5.1—5.5 τ (triplet, 2H, $>N-C\underline{H}_2-$); in dimethyl sulfoxide it showed signals at 4.82 (singlet, 1H, quinoid ring proton), 2.4—3.3 (multiplet, 4H, three aromatic and one N–H protons), and 0.55 τ (singlet, 1H, O–H proton). The hydroxy proton was assigned by the deuterium substitution method. Further clear evidence obtained from the NMR spectrum of the *O*-acetate of IV proved the presence of three aromatic protons in the ABC system.

Experimental

Materials. *p*-Benzoquinone (mp 115—116°C) was utilized by submitting a commercially-available chemical to sublimation. *n*-Butylamine, obtained commercially, was of a chemically pure grade and was used without further purification.

Separation by TLC and Instrumental Analyses.

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1) See *e.g.*, L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York (1961), p. 853.

2) J. Kumanotani, F. Kagawa, A. Hikosaka and K. Sugita, This Bulletin, **41**, 2118 (1968).

These proceedings were carried out in the same way as has already been described in a previous paper.[2]

Purification and Identification of the Products. A solution of *p*-benzoquinone (25 g, 0.232M) in 250 m*l* of 98% ethanol was stirred into a solution of *n*-butylamine (9.73 g, 0.133M) in 50 m*l* of ethanol at room temperature for 25 min. Then the solution was refluxed for 1 hr and subsequently cooled to room temperature for 1 hr under stirring. The red crystals thus precipitated were filtered off, washed with a small amount of ethanol, and dried *in vacuo*; they amounted to 5.1 g (27% of the theoretical yield). Recrystallization from dioxane gave red rod crystals, mp 163.5—164.5°C (Found: N, 11.19%). This compound was identified with an authentic sample of 2,5-bis(*n*-butylamino)-*p*-benzoquinone prepared in our laboratory.[2] When the mother liquor was evaporated to dryness at 30°C under reduced pressure, a black material was given as a residue. The light brown substance (10.7 g) obtained as an insoluble part after the black material had been washed several times with 100 m*l* of chloroform was recrystallized from water and submitted to sublimation to give white needles, mp 169.5—170.8°C. The needles were identified by comparing their IR spectrum and they showed no depression in a mixed-melting-point determination with an authentic sample of hydroquinone The solid material obtained by the removal of the chloroform from the solution under reduced pressure with an aspirator was dissolved in 60 m*l* of methanol and refrigerated for 12 hr. The crystals that precipitated were filtered off and dried *in vacuo* to yield 3.4 g (8.6%). Recrystallization from methanol and then from chloroform gave yellowish brown powders; mp 184.9—185.7°C (corr).

Found: C, 70.31; H, 7.20; N, 7.97%; mol wt, 345. Calcd for $C_{20}H_{24}O_3N_2$: C, 70.56; H, 7.11; N, 8.23%; mol wt, 340.

Derivation of the O-Acetyl Carbazolquinone. The carbazolquinone (300 mg) was dissolved in 30 m*l* of acetic anhydride, and then the solution was refluxed for 4 hr. The resulting solution was cooled and treated twice with 10 times as much as warm water (at *ca.* 50°C) to give precipitates. The crude acetate obtained by extraction with ether was dissolved in a small amount of chloroform, applied in lines on the silica-gel layers (thickness, 0 5 mm), anddeveloped with chloroform. A broad and dark brown zone at R_f 0.15—0.25 was scraped off and eluted with 30 m*l* of chloroform The elute was evaporated to dryness at room temperature under reduced pressure with an aspirator to give dark brown powders (145 mg). The powders were recrystallized from methanol; mp 147.5—149.0°C. Found: N, 7.11%; mol wt, 389. Calcd for $C_{22}H_{26}O_4N_2$: N, 7.34%; mol wt, 382. The saponification value was found to be 148.9 (*theor.* 147.4) by titrating the residual alkaline after refluxing a solution of the acetate (40 mg) dissolved in 20 m*l* of 0.05N aqueous sodium carbonate methanol (2 : 3 v/v) for 1 hr. The spectral data, *i.e.*, $\nu_{C=O}$ at 1760 cm^{-1} and the signal at 7.70 τ (3H, $-CO-C\underline{H}_3$), are in agreement with thoes of the acetate. In comparison with the NMR spectra between the acetate and its parent quinone, the three aromatic proton signals of the ABC-system are clearly seen in the range between 2 τ and 4 τ, and the proton signal of N-H is at 3.9 τ.