

Reactions of *p*-Benzoquinone Derivatives with Ethylenediamine

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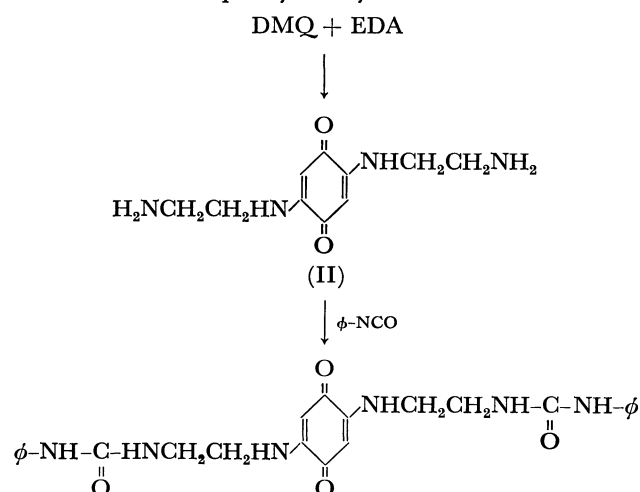
From the reaction results of *p*-benzoquinone derivatives with various amino compounds, it becomes clear that chloranil reacts with ethylenediamine to afford an unexpected product. The spectroscopic analyses of the product show that this is an addition compound with some contribution of charge-transfer structures. Bromanil gives a similar product upon reaction with ethylenediamine.

It is well known that *p*-benzoquinones react with amine derivatives. For example, *p*-benzoquinone (BQ) and 2,5-dimethoxy-*p*-benzoquinone (DMQ) react with ethanolamine (EtA) to afford 2,5-bis(2-hydroxyethylamino)-*p*-benzoquinone, and chloranil (CA) reacts with EtA to give 2,5-bis(2-hydroxyethylamino)-3,6-dichloro-*p*-benzoquinone.

Harley-Mason and Laird¹⁾ reported the successful formation of 1,2,3,4-tetrahydro-1,4,5,8-tetraazaanthracene (I) through the reaction of 2,5-dihydroxy-*p*-benzoquinone (DHQ) with ethylenediamine (EDA) by passing air into the aqueous reaction mixture. During the investigation to extend these synthetic processes to other amine derivatives, we have found that chloranil and bromanil do not afford products with the expected structures by the reaction with EDA. The present report will deal with these reactions.

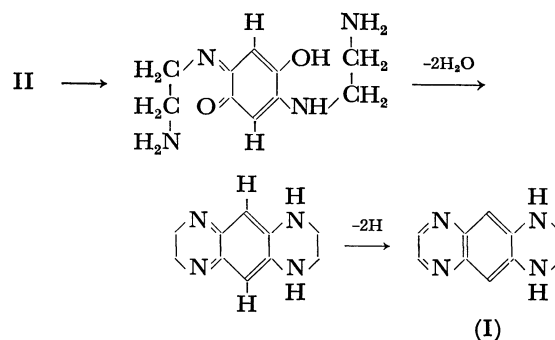
Results and Discussion

It was found that 2,5-bis(2-aminoethylamino)-*p*-benzoquinone (II) was obtained when a dispersion of DMQ and EDA in ethanol was kept overnight at room temperature. This indicates that EDA reacts with DMQ in the same way as EtA does. As II is unstable at elevated temperature, it was identified as the adduct with phenyl isocyanate.



A yellow product was obtained by heating II in water for several hours. This compound was identified as the tetraazaanthracene derivative, I, which was also prepared by Harley-Mason through another route,¹⁾ by IR and elementary analysis and by a study of its

electronic spectrum. The following reaction scheme may be supposed:



That is, II is tautomerized to an *ortho*-quinone derivative, followed by dehydration to a ring-closed product. This is unstable and is oxidized by oxygen in air to I.

Next, the reaction of CA with amines was investigated. CA reacts easily with monoacetylenediamine (AcEDA) to afford 2,5-bis(2-acetoaminoethylamino)-3,6-dichloro-*p*-benzoquinone. This product is hydrolyzed easily to chloranic acid in concentrated hydrochloric acid; therefore, the structure could be determined.

CA was dissolved homogeneously in hot benzene, and into this solution one or two equivalents of EDA in benzene were added, drop by drop. A green product(IIIa) was obtained by adding one molar equivalent of EDA, and a yellow product(IIIb) was obtained by adding two molar equivalents of EDA. These reactions were traced by means of the electronic spectra of the reaction mixtures. The CA solutions in acetone with a definite concentration were mixed with the EDA solutions in acetone in various concentrations; after the mixtures had stood for half an hour, their electronic spectra were recorded at around 380 mμ. The details of the experimental conditions and the results are listed in Fig. 1. CA has a peak at 323 mμ, and only the tail is shown in Fig. 1(No. 1). When EDA is added, a peak appears at 373 mμ; its intensity becomes greater with an increase in the concentration of EDA and attains a maximum with a slightly bathochromic effect, (5 mμ) at a molar ratio EDA/CA of unity (No. 4). By a further increase in the EDA concentration, this peak decreases in intensity and shifts to a lower wavelength, but the peak increases again in intensity at a molar ratio EDA/CA of two (No. 5).

The spectroscopic properties of the two products, IIIa and IIIb, were examined. The infrared spectra of IIIa and IIIb are similar to one another. The

1) J. Harley-Mason and A. H. Laird, *Tetrahedron*, **7**, 70 (1959).

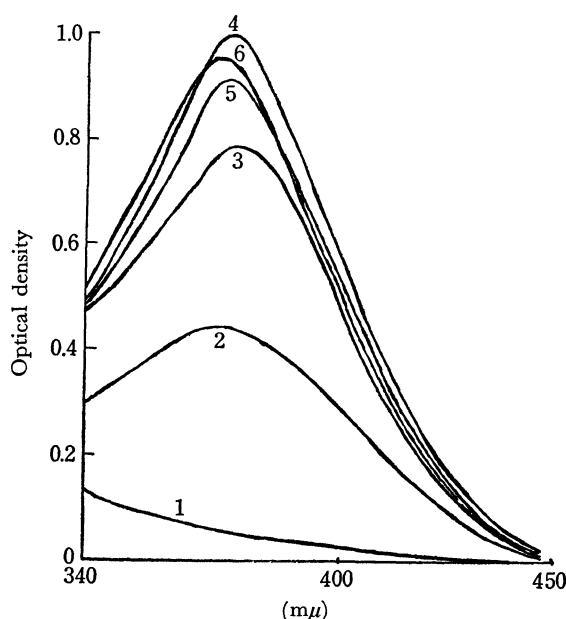


Fig. 1. Electronic spectra of the reaction of CA with EDA.

Run No.	CA(mol/l) $\times 10^4$	EDA(mol/l) $\times 10^4$
1	1.8	0
2	1.8	0.6
3	1.8	1.2
4	1.8	1.8
5	1.8	3.6
6	1.8	4.2

peaks assigned to the stretching vibrations of the $-\text{NH}_2$ and $-\text{CH}_2-$ groups and the deformation vibration of the $-\text{CH}_2-$ groups are found at 3300, 2900, and 1420 cm^{-1} respectively, but no peak assigned to $>\text{C}=\text{O}$ is clearly found.

The proton NMR spectra of EDA, IIIa, and IIIb were obtained at 60 MHz in dimethyl sulfoxide- d_6 , with reference to tetramethylsilane as the internal standard. The peaks of protons of the $-\text{CH}_2-$ and $-\text{NH}_2$ groups of EDA are found at 2.50 and 1.30 ppm; those of IIIa, at 3.27 and 7.68 ppm, and of IIIb at 2.82 and 6.13 ppm, respectively. The peaks of $-\text{NH}_2$ were determined by adding deuterium oxide. The intensity ratio of the $-\text{NH}_2$ to the $-\text{CH}_2-$ group, however, is not equal in the spectra of IIIa and IIIb, probably because of the presence of a small amount of water in the solvent.

In the mass spectrum of IIIa, the m/e value of the parent ion is 246; this is equal to the value referred to CA, and the spectrum pattern is similar to that of CA. In the mass spectrum of IIIb, the parent ion is m/e 248 and the spectrum pattern is very similar to that of tetrachlorohydroquinone (TCHQ).

Moreover, the following result was obtained. IIIb reacts with acetic anhydride in the presence of pyridine as a catalyst to afford tetrachlorohydroquinone diacetate. It is clear from IR and elementary analysis that this product is the same as the compound obtained by the acetylation of TCHQ with acetyl chloride in pyridine.

Similar behavior was observed for bromanil (BA). That is, while BA reacts with AcEDA to give 2,5-bis(2-acetoaminoethylamino)-3,6-dibromo-*p*-benzo-

quinone, it does not react with EDA to afford the expected product; instead, IVb is obtained from the mixture. This product reacts with acetic anhydride to afford tetrabromohydroquinone diacetate, as in the case of CA.

These investigations lead to the following interesting conclusion. While CA and BA react easily with aliphatic and aromatic amines, they react with EDA to afford unexpected addition products. The structures of these addition compounds, IIIb and IVb, could not be definitely determined from these results, but they might be similar to those of the reaction intermediates in reactions of CA and aromatic amines examined by Nagakura *et al.*²⁾ The reaction properties of CA described above are in accord with the result that the reaction of CA and *o*-phenylenediamine does not give a well-defined product, unlike the reactions with *m*- and *p*-phenylenediamine.

Experimental

2,5-Bis(2-aminoethylamino)-*p*-benzoquinone (II). Four grams of DMQ and 16 g of EDA were dispersed in 200 ml of ethanol, and the mixture was then left standing overnight. By filtration, a red-violet solid was obtained as the product (II); yield, 6 g. The product (0.3 g) was dissolved in 50 ml of DMF, then after which 1 ml of phenyl isocyanate was added. The reaction mixture was heated at 100°C for one hour, and then cooled and poured into water. The dispersed solid was collected, dried, and recrystallized from acetic acid; mp 254°C .

Found: C, 62.05; H, 5.77; N, 18.07%. Calcd for $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_6$: C, 62.33; H, 5.67; N, 18.17%.

1,2,3,4-Tetrahydro-1,4,5,8-tetraazaanthracene (I). One gram of II was dispersed in 300 ml of water, and the mixture was refluxed for ten hours. Water was removed under reduced pressure, and the yellow residue was recrystallized from nitrobenzene to afford yellow needles.

Found: C, 64.46; H, 5.29; N, 30.04%. Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_4$: C, 64.50; H, 5.41; N, 30.09%.

2,5-Bis(2-acetoaminoethylamino)-3,6-dichloro-*p*-benzoquinone.

A mixture of 10 g of CA and 20 g of AcEDA in 200 ml of ethanol was refluxed for five hours. After cooling, the dispersed solid was collected by filtration and dried; crude yield, 15 g (98%). It was recrystallized from a mixture of pyridine and water. mp 246°C .

Found: C, 44.77; H, 4.70; N, 14.88%. Calcd for $\text{C}_{14}\text{H}_{18}\text{N}_4\text{Cl}_2\text{O}_4$: C, 44.56; H, 4.77; N, 14.85%.

The Reaction Product from CA and One Mole Equivalent of EDA (IIIa).

Five grams of CA were dissolved in 100 ml of hot benzene, and into the resulting solution 2.44 g of EDA in 50 ml of benzene were added, drop by drop. Green solids separated out immediately. The hot mixture was filtered to collect a solid product, which was then dried under reduced pressure; yield, 6.5 g.

Found: C, 20.99; H, 2.19; N, 8.00; Cl, 40.48%.

The Reaction Product from CA and Two Mole Equivalents of EDA (IIIb).

Five grams of CA and 4.88 g of EDA were mixed in a way similar to that used in the case of IIIa; yield, 9.2 g.

Found: C, 33.39; H, 3.43; N, 15.00; Cl, 36.00%. Calcd for $\text{C}_{10}\text{H}_{16}\text{N}_4\text{Cl}_4\text{O}_2$: C, 32.81; H, 4.41; N, 15.31; Cl, 38.74%.

2) T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969).

The Reaction Product from BA and Two Mole Equivalents of EDA (IVb). Into 8.6 g of BA in 120 ml of hot benzene,

4.88 g of EDA in 50 ml of benzene were added; yield, 6.5 g.

Found: C, 22.55; H, 2.37; N, 8.11; Br, 56.84%. Calcd for $C_{10}H_{16}N_4Br_4O_2$: C, 22.02; H, 2.97; N, 10.30; Br, 58.77%.

Tetrachlorohydroquinone Diacetate. One gram of IIIb and a few drops of pyridine were added to 10 ml of acetic anhydride, and the mixture was heated at 40°C for three hours. The reaction mixture was poured into water, and the pre-

cipitates were collected by filtration and recrystallized from a mixture of dioxane and water; mp, 247°C (lit. 252°C).

Found: C, 36.30; H, 1.53; Cl, 42.52%. Calcd for $C_{10}H_6Cl_4O_4$: C, 36.14; H, 1.81; Cl, 42.77%.

Tetrabromohydroquinone Diacetate. This was prepared from IVb and acetic anhydride and was recrystallized from acetic acid; mp 284°C (lit. 283°C).

Found: C, 23.88; H, 0.89; Br, 61.88%. Calcd for $C_{10}H_6Br_4O_4$: C, 23.56; H, 1.19; Br, 62.69%.
