

Reaction of Quinones with Nitrosoarenes

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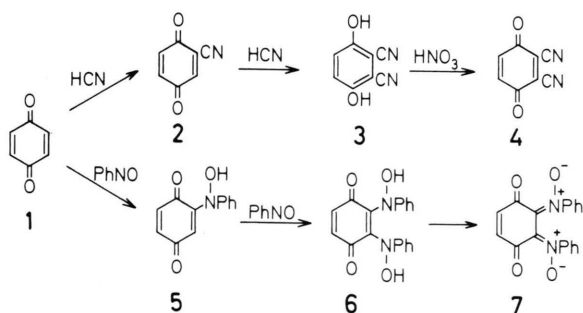
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Addition, Nitrosobenzene, 4-Benzoquinone, Nitroxide, Trap

The structure of the dinitrone formed on reaction of nitrosobenzene with 1,4-benzoquinone has been confirmed by spectroscopic measurements. An electron transfer radical-anion mechanism is suggested to account for its formation.

Introduction

Nucleophilic addition to 1,4-benzoquinone (**1**) usually yields a 2,5-disubstituted benzoquinone [1]. In this respect addition of hydrogen cyanide [2] and nitrosobenzene [3] appear to be anomalous. Both are reported to give 2,3-disubstituted products, the latter giving **7** presumably *via* the hydroxylamines **5** and **6**.



Formation of the 2,3-dicyanohydroquinone (**3**) can be rationalised in terms of preferential addition of cyanide at the most electron deficient unsubstituted carbon of the cyanoquinone (**2**) in the same way as alcohols and other nucleophiles add to the 3-position of the acylquinone (**8**) [4]. However, such an argument could not be applied to the formation of the dihydroxylamine (**6**). Hence, either the structure of the product **7** is incorrect or it is not formed by a stepwise nucleophilic addition process. We have now investigated these alternatives.

Structure

The structure assigned to **7** by Gündel and Pummerer [3] was based mainly on elemental analysis

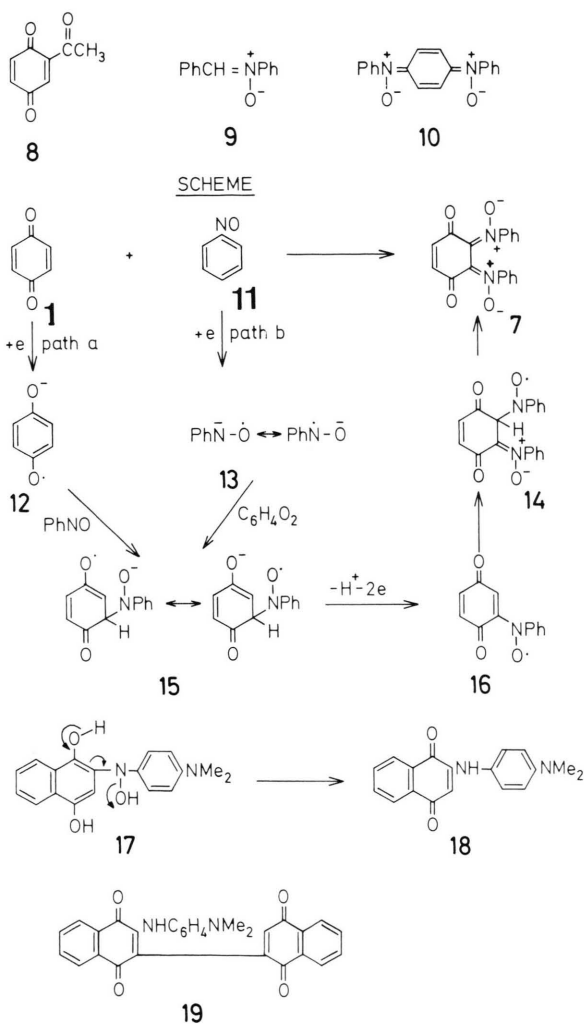
and reduction to the corresponding dianilinohydroquinone which gave a dihydrobenzimidazole on treatment with acetic anhydride and a benzdi(oxazolone) with phosgene. We confirm that the spectral characteristics of the product are in accord with this assignment. Thus, its IR spectrum shows carbonyl absorption at 1660–1650 cm⁻¹ and no absorption >3050 cm⁻¹. The ¹H NMR spectrum shows signals from only quinonoid (2H, sharp singlet) and aromatic (10H, multiplet) protons at δ 6.76 and 7.7–7.25, respectively. A symmetrical structure was also indicated by its ¹³C NMR spectrum which had signals from only seven different carbons. Those at δ 177.8, 149.2 and 137.9 were assigned to carbonyl, nitrone, and olefinic carbons, respectively and confirmed by an off-resonance experiment. In the ¹⁴N NMR spectrum only one signal at 104 ± 5 ppm (relative to nitromethane) was detected (this lies midway between that from the mononitron **9** at 118 ± 5 ppm and dinitron **10** at 90 ± 10 ppm) thus confirming the presence of identical nitrogen atoms. Finally, the mass spectrum (C₁₈H₁₂N₂O₄, accurate mass measurement) showed the expected loss of one and two oxygens and one and two phenyls from the molecular ion.

Mechanism

When an ethanolic solution of benzoquinone and nitrosobenzene is placed in the cavity of an ESR spectrometer the spectrum of a nitrogen centred radical (a_N = 10.8 G) slowly develops (Fig. 1). This signal not only persists but intensifies throughout the course of reaction. No other radical or radical-ion was detected. Further, the reaction proceeds relatively well in alcoholic solvents (25% in ethylene glycol, 25% in isopropanol, 17% in *t*-butanol, 15% in ethanol) less well in dipolar solvents such as dimethyl sulphoxide (13%), poorly in acetonitrile (4%) and acetone (trace) and not at all in chloroform (ethanol-free), methylene dichloride and benzene. The obser-

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variations strongly indicate that the reaction is a radical process involving electron transfer. Accordingly the following scheme is proposed in which **15** and **16** are key intermediates.

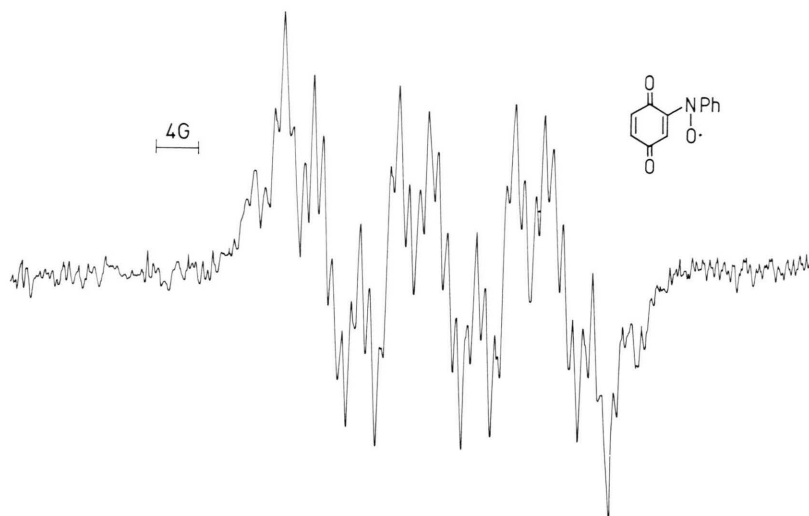


Reaction is initiated by formation of catalytic amounts of either radical-anion **12** or **13** which is trapped by either nitrosobenzene or benzoquinone, respectively, to give the intermediate **15**. Initiation is not caused by photo-reduction since direct sunlight had no effect on the rate of initiation. At this point the two paths converge and **15** is oxidised to the quinonoid nitroxide **16** which in turn is trapped by reaction with a second molecule of nitrosobenzene to give **14** a readily oxidised intermediate. The intermediate **15** and its oxidation can be depicted in a

number of ways and only one possibility is shown here but formation of the quinonoid nitroxide **16** is necessary to lead to vicinal disubstitution in the final product **7**. The oxidations **15**→**16** and **14**→**7** could in principle be affected either by nitrosobenzene or benzoquinone. Measurement of half-wave potentials of benzoquinone and nitrosobenzene under the conditions of the reaction have not been made but existing data suggest that benzoquinone [5, 6] ($E_{1/2} = -0.15$ V, DMF, Ag/AgCl, $\text{Et}_4\text{N}^+\text{ClO}_4^-$) is more easily reduced than is nitrosobenzene [7] ($E_{p1} = -0.37$ V, DMF, Ag/AgI, $\text{Bu}_4\text{N}^+\text{BF}_4^-$) although the comparison is not exact.

Consistent with the Scheme are the following observations. (i) When 1,4-benzoquinone is replaced by quinol or nitrosobenzene by phenylhydroxylamine the dinitrone **7** is not formed. (ii) Exclusion of air has only a small effect on the overall yield of product (**15**→**11**%). Oxygen, since it will oxidise semiquinone to quinone, should increase the extent of reaction and hence the yield of **7**. (iii) Addition of a few drops of dilute hydrochloric acid to the reaction mixture did not significantly alter the course of the reaction but similar addition of alkali caused major decomposition. (iv) The ESR spectrum detected has been interpreted as follows $a_N = 10.8$ G, $a_H = 5.2$ G (1H), $a_H = 2.7$ G (3H), $a_H = 0.85$ G (2H) which gives good correspondence with line positions. However, the experimental spectrum is not fully resolved and there are differences in line intensities between experimental and theoretical spectra. Nevertheless, there is no doubt that the spectrum is that of a phenyl nitroxide in which there is a major splitting with one additional proton. The most likely candidate is the nitroxide **16**. (v) One of the intermediates detected by TLC gave a positive tetrazolium test [8] indicating the presence of the hydroxylamino group. (vi) A better yield of dinitrone corresponding to **7** was obtained when 2,3-dichloroquinone replaced benzoquinone. This dichloroquinone is a better oxidant than is 1,4-benzoquinone.

Reaction of 1,4-naphthoquinone and *p*-dimethylaminonitrosobenzene in alcohol did not lead to the formation of a dinitrone corresponding to **7**. Instead, the known arylaminonaphthoquinone **18** [9] and the biquinone **19** [$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4$ (ms), δ 7.25 (s) (1H—QH proton), ν_{max} 3305, 1670, 1660 cm^{-1}] were isolated after chromatography of a complex reaction mixture. This contrasts with the experience of Gündel and Pummerer who reported a low yield of the



dinitrone corresponding to **7** but provided few details. Formation of **18** by dehydration of **17** is easily envisaged and **18** is clearly an intermediate *en route* to the diquinone **19**. This example illustrates well the potential complexity of reactions of quinones with nitrosoarenes the course of which is likely to be determined by the redox properties of the participating quinone and nitrosoarene.

Experimental

N,N'-(Cyclohex-2-enyl)-4,5-diylidene-1,4-dione-di(phenylamino)*N,N'*-Dioxide (**7**)

In a typical experiment a solution of 1,4-benzoquinone (200 mg) and nitrosobenzene (200 mg) in ethanol (20 ml) was left at room temperature for 28 d. The product, which had precipitated, was collected and crystallised from ethanol giving dark brown shining plates, m.p. 178–180 °C.

IR cm^{-1} (Nujol mull): 1660 (C=O); $^1\text{H NMR}$ (CDCl_3): δ 6.76 (2H, s, CH=CH), 7.25–7.70 (10H, m, ArH); $^{13}\text{C NMR}$ (CDCl_3): δ 177.8 (C=O), 149.2 (C=N), 137.9 (CH=CH), 135.9, 131.08, 128.94, 124.6 (all aryl C); *MS* m/z (rel. int.): 320(M^+)(4), 304(4), 288(10), 227(50), 211(5), 197(13), 183(5), 124(67), 103(22), 91(10), 82(79), 77(100).

Precise mass for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_4$

Calcd 320.0797,
Found 320.0796.

Reaction of *p*-nitrosodimethylaniline with 1,4-naphthoquinone

Naphthoquinone (3.16 g) and *p*-nitrosodimethylaniline (3.0 g) in ethanol (60 ml) were left to react at

room temperature for 23 d. After removal of solvent, the residue was chromatographed (plc) (twice) on silica gel HF₂₅₄ using butanone:hexane (1:4) as eluant to give.

(i) 2-*p*-Dimethylaminophenylamino-1,4-naphthoquinone (**8**) as purple needles, m.p. 202–203 °C (from chloroform-hexane).

UV nm (EtOH): 210, 246 (sh), 280, 540; *IR* cm^{-1} (Nujol mull): 3275 (NH), 1680 (C=O); $^1\text{H NMR}$ (CDCl_3): δ 2.95 (6H, s, 2Me), 6.2 (1H, s, 3-H), 6.4–7.2 (4H, m, C_6H_4), 7.3–7.8 (3H, m, 2 ArH+NH), 8.1 (2H, d, 5- and 8-H); *MS* m/z (rel. int.): 292(M^+)(100), 276(5), 248(4), 146(11), 145(13), 105(9), 85(56), 83(79).

Precise mass for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$

Calcd 292.1211,
Found 292.1213.

(ii) 3-(*p*-Dimethylaminophenylamino)-2,2'-bi(1,4-naphthoquinonyl) (**19**) as brown needles, m.p. 210–212 °C (decomp.) (from chloroform-hexane).

IR cm^{-1} (Nujol mull): 3305 (NH), 1670, 1660 (C=O); $^1\text{H NMR}$ (CDCl_3): δ 2.5 (6H, s, 2Me), 6.4 (s, 1H, 3'-H), 6.13 and 6.75 (4H, m, C_6H_4), 7.5–8.2 (9H, m, ArH+NH); *MS* m/z (rel. int.): 448(M^+)(100), 432(11), 420(13), 401(5), 392(5), 376(6), 314(63), 274(9), 202(13), 135(79), 121(56), 105(18).

Precise mass for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4$

Calcd 448.1422,
Found 448.1422.

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