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THE HYDROCYANATION OF FREE AND POLYMER-BOUND BENZOQUINONE

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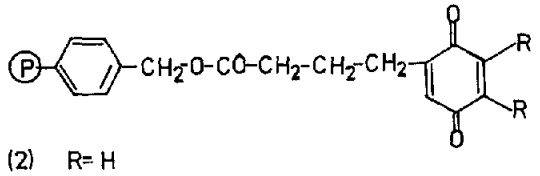
Abstract—The polymer-bound quinone **2** has been prepared and used in column form with organic solvents for the convenient preparation of other quinones. In contrast to the solution reaction hydrocyanation of this quinone by the Thiele–Meisenheimer reaction did not yield a useful proportion of polymer-bound dicyanohydroquinone but instead gave a mixture of products including much monocyanohydroquinone. Helferich and Bodenbender's 2,3-dicyanocyclohexan-1,4-dione is in fact wholly the di-enol and is a likely intermediate in the hydrocyanation of benzoquinone, being oxidised by the latter to 2,3-dicyanocyclohex-2-ene-1,4-dione which tautomerises to the observed product, 2,3-dicyanohydroquinone. A lower accessibility to polymer-bound reactants as compared with those in solution is implied by these results.

In recent years, solid phase synthesis[1] and in particular the development of polymer-bound reagents[2] has allowed considerable simplification of various difficult work-up procedures with consequent gains in yields and in saving time. For the preparation of certain sensitive quinones, we hoped to prepare a high-potential quinone attached to an insoluble polymer by a spacer group and to use this material repeatedly in chromatographic columns to convert solutions of quinols in organic solvents to eluates of the required quinones.

The concept of an oxidation reduction (redox) resin or electron-exchange polymer appeared in 1949 and initiated their development by Cassidy,[3] Kun,[4] Manecke[5] and others concurrently with that of other solid phase reagents and supported substrates.[1] A number of redox systems have been incorporated in such polymers, the quinone–hydroquinone redox system being the most studied. This type has been synthesized by methods[3,5] which have provided a wide variety in both polymer and quinone with the redox systems either incorporated in the strands or attached closely to them. Various of these products have been shown to be useful for oxidation reduction of inorganic ions, deoxygenation of aqueous solutions and other purposes. The goal of hydrophilicity and the acceptability of low redox potentials resulted in products generally not suitable to our purposes although applications to the dehydrogenation of tetrahydronaphthalene, hydrazobenzene, etc. have been reported.[3]

An exploratory preparation of a polymer-bound hydroquinone (**1**) oxidizable to a useful quinone (**2**) of moderate redox potential was readily achieved. The triethylammonium salt of 4-(2′,5′-dihydroxyphenyl) butanoic acid was coupled with a chloromethylated (*ca.* 1.8 meq/g) polystyrene (Biobeads SX–2) to yield the polymer-bound hydroquinone (**1**) of loading *ca.* 1.0 mmol/g polymer.



(2) R= H

(3) R= CN

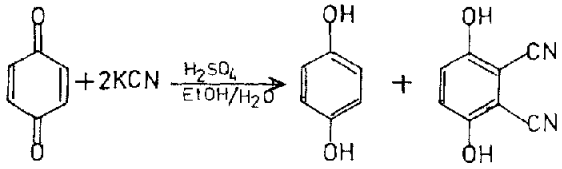
Ceric ammonium nitrate in buffered aqueous acetonitrile conveniently oxidised **1** to stable yellow beads of the polymer-bound benzoquinone **2** showing quinone and ester carbonyl stretching at 1655 and 1730 cm^{-1}, and a redox capacity of *ca.* 1.0 mmol/g polymer with a redox potential presumably similar to that of methylbenzoquinone. This polymer, as a column, efficiently prepared low-potential quinones e.g. di-, tri- and tetramethylbenzoquinones, 1,4-naphthoquinones and others from the quinols in essentially quantitative yield, the products being isolated by evaporation of the eluates. Methyl 1,4-naphthoquinone-2-carboxylate was prepared using a column containing two moles of resin quinone, in higher yield and more conveniently than by the use of DDQ. Five oxidation/reduction cycles of the quinone resin resulted in negligible loss of redox capacity. During oxidations in columns flowing under gravity, the lower yellow zone of the quinone polymer and the upper tan-colored zone of the resulting hydroquinone polymer were usually separated by a narrow green zone, presumably of mixed quinhydrones, so that the extent of the reduction of the column was immediately recognisable during reactions. Further, a polymer-bound quinone used in column form should achieve a more complete oxidation of a hydroquinone of similar redox potential than it would if used by equilibration in a suspension. The column certainly effects more rapid reaction.

Since the immobilization of a higher potential quinone appeared to promise the desired reagent, 4-(3′,4′-dicyano-2′, 5′-dihydroxyphenyl)-butanoic acid was coupled with chloromethylated polystyrene but the oxidized product produced little benzoquinone from (**4**). High potential sulfonylquinones appeared to offer another approach but attempts to reduce polystyrene-sulfonic acid to the sulfinic acid (to enable direct coupling of quinones to resins by sulphone linkages) via the sulfonyl chloride failed under conditions which were successful with toluene-p-sulfonyl chloride itself.

The direct cyanation of the quinone (**2**) by the base-catalysed variant of the Thiele–Meisenheimer reaction was also attempted. In the presence of even catalytic quantities of potassium cyanide, the hydrocyanation of benzoquinone to 2,3-dicyanohydroquinone proceeds rapidly with liquid hydrogen cyanide in acetonitrile and very rapidly in DMSO. Stirring (**2**) with excess hydrogen

cyanide in DMSO or acetonitrile in the presence of potassium cyanide yielded brown beads showing infrared absorption for hydroxyl, cyanide and carbonyl groups. The oxidation of this preparation with ceric ion or nitrogen oxides did not provide a substantial yield of the desired polymer-bound quinone (3).

In view of this result, we investigated certain aspects of the Thiele–Meisenheimer addition of cyanide to benzoquinone itself. It has been asserted[6] that under optimum conditions, this reaction yields a 1:1 mole ratio of hydroquinone (4) and 2,3-dicyanohydroquinone (5) and also that 2-cyano-1,4-hydroquinone (6) and 2-cyanobenzoquinone[7] (7) cannot be detected among the products. The reaction is thus unusual amongst nucleophilic additions to quinones in yielding a 2,3-disubstituted hydroquinone rather than a monosubstituted hydroquinone or a 2,5-disubstituted benzoquinone.



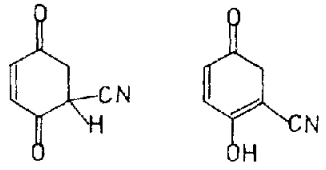
(4) (5)

In 1941, Allen and Wilson[8] suggested the sequence of reactions shown in Scheme 1, invoking the greater reactivity of unsaturated nitriles relative to enones, as the factor leading to 2,3-disubstitution.

Wallenfels, Bachmann, Hofmann and Kern[6] in 1965 criticized the suggested oxidation of (6) to (7) by benzoquinone as thermodynamically unacceptable (adverse potential, 210 mV) and considered that the moisture-sensitive quinone (7) would in any case be destroyed in the reaction medium. A further possibility, that cyanogen (from the oxidation of cyanide ion) adds to benzoquinone, was briefly stated to have been excluded. Wallenfels *et al.*[6] proposed Scheme 2, ascribing the 2,3-disubstitution in (5) to a lower activation energy for terminal addition of cyanide ion to the dienone system of (8) as compared to the 1,4-addition. However, 1977, Nagata and Yoshioka[9] suggested again that the reaction proceeds by way of (7) formed by autoxidation of (6).

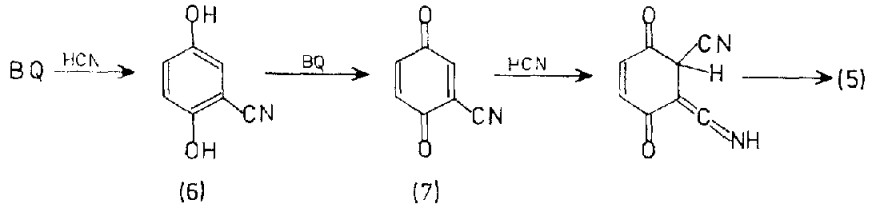
We found by hplc analysis of reaction mixtures from hydrocyanation of benzoquinone under various conditions, that (amongst other minor signals) peaks for (6) are obtained which correspond to yields of up to 6%. From the reaction carried out as prescribed by Wallenfels *et al.*, 2.5% of crystalline 2,5-dimethoxybenzonitrile was obtained by chromatographing the methylated mother liquors of (5) on silica gel. Products from benzoquinone and HCN/KCN in acetonitrile or DMSO, and from KCN alone in the latter solvent, provided hplc and/or glc evidence for (6) in yields up to 4% in addition up to 80% of (5) and (4). Hence monocyanohydroquinone (6) is produced in the Thiele–Meisenheimer reaction and also in its base-catalysed version although only to a minor extent. The presence of (6) is consistent with (8) being formed as the first intermediate, a reaction analogous to that of benzoquinone with other nucleophiles.

The proposal of Wallenfels *et al.*[6] requires that a second cyanide ion adds rapidly to the carbon terminal of the dienone system of (8) to give (9), thereby largely preventing enolization of (8) to the aromatic (6) or ketonization of the terminal enol of (8) to give the enedione (10) (which itself would yield (6) by way of (11)). While 1,6-addition involves attack at the most electron deficient carbon and presumably provides better electron delocalization in the transition state, it is this step (in the Wallenfels interpretation) which distinguishes the Thiele–Meisenheimer reaction from other examples of nucleophilic additions to benzoquinone.



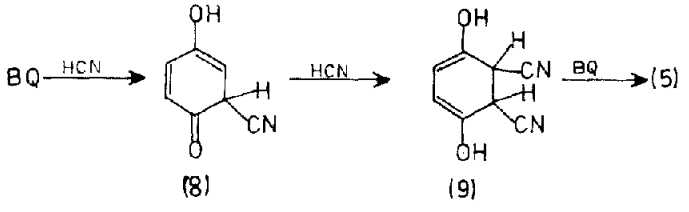
(10) (11)

It is shown below that the formation of (9) would lead to the observed outcome by the route shown in Scheme 3



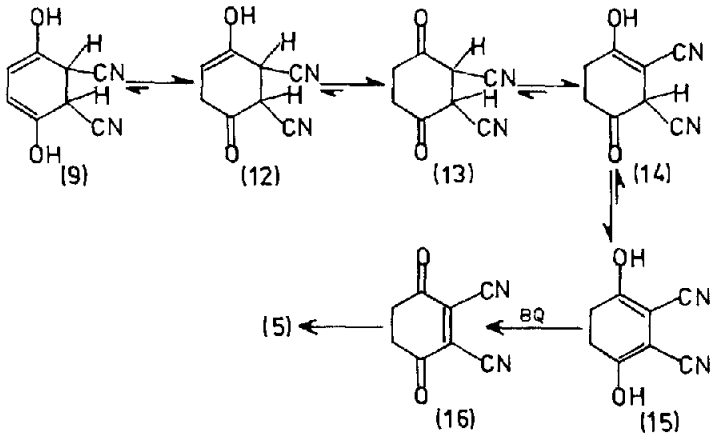
(6) (7)

Scheme 1.



(8) (9)

Scheme 2.



Scheme 3.

and our observations on the hydrocyanation products of the polymer-bound quinone (2), as described below, provide further support for this view.

The Wallenfels intermediate (9) would clearly be unstable relative to (12) and the diketone (13), which will readily enolize to (14) and (15). Other tautomers may also be involved but (15) should predominate in this sequence of equilibria since, while 2-cyanocyclohexanone equilibrates with only 20% of its enol,[10] (15) is further favoured by its conjugated diene system.

The diketo structure (13) was assigned by Helferich and Bodenbender[11] in 1921 to a product obtained by the reduction of (5) with sodium in aqueous sodium hydroxide. Our preparation of this product yielded colorless crystals, decomposing at 164°, which showed slow aerial oxidation in solution to (5). The strong ultraviolet absorption of this product was not consistent with structure (13). A PMR singlet at δ2.54, strong hydroxyl absorption at 3125 cm^{-1} and bands at 2225, 1635 and 720 cm^{-1} for nitrile and olefinic bonds suggest (15) rather than (13). No evidence for (12), (13) or (14) could be seen in the PMR spectra of this reduction product. It yielded a diacetate m.p. 162.5–164° which showed singlets at δ2.54 (4H) and at δ2.3 ($COCH_3$) but is known[11] to form a disemicarbazone which is presumably a derivative of (13).

For (15) to be considered as an intermediate in the hydrocyanation of benzoquinone to 2,3-dicyanohydroquinone (5), it must be oxidizable by benzoquinone. Addition of molar benzoquinone to (15) in $CDCl_3$ causes the immediate appearance of PMR singals for hydroquinone. A singlet at δ3.10 replaces that of (15) at δ2.54. This change is consistent with the oxidation of (15) to (16), which is also brought about by nitrogen oxides, the product being stable to excess of either oxidant. Under neutral conditions, the PMR signals for (15) only slowly (30 min) to give place to those of (5). Hydrochloric (but not acetic) acid effects the change immediately. In some particular hydrocyanation reactions it was noticed that the production of (5) appeared to continue slowly during work-up, possibly from aerial oxidation of (15) in the absence of benzoquinone.

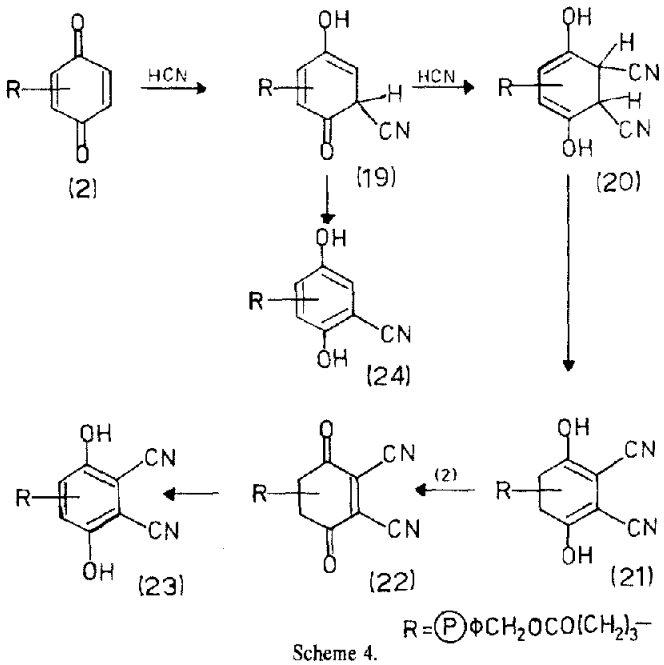
The enedione (16) could not be isolated, only (5) resulting from various attempts. Evidence for its presence was obtained by adding cyclopentadiene to its yellow solution, Immediate decolorization resulted and was followed by precipitation of a Diels–Alder product, (17), $C_{13}H_{10}N_2O_2$, of double m.p. 149° and 260°. The IR spectrum was consistent with the presence of cyano and keto groups and unsaturation. The PMR spectrum consisted of a 10 Hz doublet (2H) AB quartet at δ3.92 and a broad singlet (2H) at δ6.32. Structure (17) is appropriate to a derivation from (16), the spectral evidence and the formation of a closely analogous product, (18), $C_{13}H_8N_2O_2$ from 2,3-dicyanobenzoquinone and cyclopentadiene, with double melting point 136° and 256°. The PMR spectra are similar, apart from differences (the AA'BB' 4H system vs 2H singlet at δ6.84) which confirm the relationship of the two adducts. While in (17), the cyano groups would be expected[12] to be *endo*, the case of (18) is ambiguous. The very similar melting point behaviour argues for a similar *endo* structure.

The reactions of (15) and (16) are therefore fully consistent with their proposed roles as intermediates in the hydrocyanation of benzoquinone. With Wallenfels' intermediate dienol (9), they take their place in a logical sequence of intermediates between the first addition of cyanide ion and the final product, 2,3-dicyanohydroquinone.

Returning to the hydrocyanation of the polymer-bound quinone (2), it would be anticipated that the dihydroaromatic dinitrile (21) would be formed as in Scheme 4 but not oxidised to (22) if polymer-bound reactants are as isolated as has often been implied.[13] Detailed study showed that neither (21) nor the desired dicyanohydroquinone (23) predominated in our hydrocyanated quinone polymer.

For revealing the nature of the products of the hydrocyanation of the polymer-bound quinones, elemental analysis and IR spectra proved inadequate but vital information was obtained by measuring the redox capacity of the resin to benzoquinone and trimethylhydroquinone.

Polymer-bound hydroquinone (1.03 mmol/g), was oxi-



Scheme 4.

dised to the quinone resin (**2**) which titrated for 1.03 mmol/g of quinone when equilibrated with trimethylhydroquinone. A sample (A) of this quinone (**2**), suspended in a DMSO solution of hydrogen cyanide, was stirred with a catalytic quantity of potassium cyanide at room temperature for 12 h. Filtration and thorough washing gave a brown product (B). Elemental analysis showed an increase of 1.0 mg atoms per g in the nitrogen content. The infrared spectra of (B) showed bands at 3400, 2175, 1730 and 1650 cm^{-1} assignable to hydroxy, cyanide and carbonyl groups.

Product (B) equilibrated with benzoquinone, yielded (C) and 0.33 mmol/g of hydroquinone, which represents the sum of the hydroquinone polymer (**1**) and of the di-enol (**21**) formed during hydrocyanation. Product (B) equilibrated with trimethylhydroquinone yielded 0.15 mmol/g of trimethylbenzoquinone resulting from oxidation by the residual quinone (**2**) in (B). Sample (C) was also equilibrated with trimethylhydroquinone yielded 0.35 mmol/g of trimethylbenzoquinone due to residual (**2**) not changed during the hydrocyanation plus (**2**) resulting from the oxidation of the (**1**) which was formed during the hydrocyanation. Now assuming that oxidation of the di-enol (**21**) to the enedione (**22**) was the only source of (**1**) in the hydrocyanation product and that trimethylbenzoquinone lacks the potential to oxidise (**21**) to (**22**), then the quantities of the various products in mmol/g are (**1**), 0.20; (**2**), 0.15; bound dicyanohydroquinone (**23**) (from **22**), 0.20 and di-enol (**21**), 0.13. From this data we are able to conclude (a) that diycano-products, (**21**) and **23**) totalled 0.33 mmol/g, (b) that 0.68 mmol/g (i.e. 1.03–0.35) of quinone reacted with HCN and therefore that 0.35 mmol/g (0.68–0.33) of quinone (**2**) are not accounted for.

Assigning 0.66 of the 1.0 mg atoms of the additional nitrogen present to the 0.33 mmol of dicyano products, a residue of 0.34 mg atoms of nitrogen remains, in agreement with the 0.35 mmol of missing quinone. We conclude that the 0.35 mmol/g of quinone (A) was converted to monocyanohydroquinone (**24**) by aromatization of the monocyano-intermediate (**19**). The elemental analysis data (C, H, O, N, Cl) for the hydrocyanation product (B) agreed within accepted limits with calculated values for the above composition after allowing for residues of bound benzyl chloride, etc. Although infrared difference spectra were used to emphasise the changes between the various polymers, it was possible to conclude from these only that the observed spectra were not inconsistent with the presence of bound hydroquinone, quinone, cyanohydroquinone, dicyanohydroquinone and di-enol in the hydrocyanated resin.

The hydrocyanation of the quinone resin is therefore interpreted as paralleling that of free benzoquinone in sequence but producing products in different proportions. Thus *ca.* 60% of the bound quinone reacted with HCN, *ca.* 32% reacting twice to give di-enol (**21**) and *ca.* 19% being further oxidized and enolized to bound dicyanohydroquinone (**23**). Of the bound benzoquinone, *ca.* 15% remained unchanged and *ca.* 19% was reduced in oxidising the di-enol (**21**). Significantly, *ca.* 34% was converted to the bound monocyanohydroquinone (**24**) in contrast to the low yields obtained in the solution reactions of benzoquinone itself. Clearly, in the polymer, enolization of the intermediate (**19**) is favoured, probably by the slow delivery of the second cyanide ion to the site of reaction.

The use of a more rigid macroporous polystyrene (Dow XFS 4022) support resulted in relatively higher yields (*ca.* 45%) of bound monocyanohydroquinone, significantly less intrapolymeric oxidation (*ca.* 7%), reduced capacity and the hampering of infrared analysis by the strong carbonyl bands characteristic of the resin as supplied.

A consistent picture thus emerges for the hydrocyanation of free and polymer-bound 1, 4-benzoquinones. The results also emphasize that access of reagents to polymerbound reactants may be restricted to the extent of modifying the course of reactions as observed in solutions. Site-site isolation was not a determining influence in the reactions examined. The demonstrated utility of our

recyclable polymer-bound quinone of moderate potential has further enhanced the attractiveness of a high potential polymer-bound quinone as an organic reagent.

EXPERIMENTAL

General

Microanalyses are by J. C. Kent and P. Nobbs of this Chemistry Department and the CSIRO Microanalytical Service, Melbourne. Melting points are uncorrected. ^{1}H NMR spectra were recorded at 100 MHz with Jeol MH-100 and PS-100 instruments. and mass spectra at 70 eV with an A.E.I. MS902S instrument. IR spectra were obtained from Nujol mulls or KCl discs containing a *ca.* 2% admixture of polymer using a Perkin-Elmer Infracord 237.

Preparation and use of polymer-bound quinone (2)

4-(2', 5'-Benzoquinonyl)butanoic acid. Succinoylation of 1, 4-dimethoxybenzene in 1,2-dichloroethane gave 3-(2'-5'-dimethoxy benzoyl)propanoic acid in varying yields up to 60%, rather than the 97% reported by Beraudiat *et al.*[14] This product was demethylated by refluxing in aq HBr (48%) for 15 min and hydrogenated over 10% Pd/C in AcOH at 65° to give 4-(2'-5'-dihydroxyphenyl)butanoic acid in 90% overall yield. Recrystallization from EtOAc/hexane gave colourless crystals, m.p. 131–132° (lit.[15] 131–132°). The hydroxy compound was oxidized to the quinone with $NaClO_4/VO_5$ in dilute sulfuric acid or ceric ammonium nitrate in aqueous MeCN.[16] Recrystallization from toluene gave yellow crystals, m.p. 109–110° of the benzoquinonylbutanoic acid (lit.[15] 105°).

Coupling of 4-(2', 5'-dihydroxyphenyl)butanoic acid with polymer. The chloromethylated SX-2 resin (6.4% Cl) (10 g) and 4-(2'-5'-dihydroxyphenyl)-butanoic acid (3.72 g) were suspended in EtOH under N_2. Triethylamine (1.92 g) was added and the mixture stirred under reflux for 43 h. The resin was filtered, washed extensively and dried *in vacuo* to give the hydroquinone resin as light tan beads (Found: C, 81.6; H, 7.6; N, 0.7; O, 6.7; Cl, 2.4%). IR (KCl) 3400, 1730 cm^{-1}.

Polymer-bound quinone (2). The hydroquinone resin (10 g) was stirred with ceric ammonium nitrate (14 g) and NaOAc (5 g) in aqueous CH_3CN for 0.5 hr, filtered and washed extensively to give the quinone resin **2** as yellow beads (Found, C, 80.9; H, 7.4; N, 0.6; O, 6.8; Cl, 0.3%). IR (KCl) 1730, 1655–1600 cm^{-1}.

Oxidations with the polymer-bound quinone (2). (a) The resin (1–5 g) was suspended in MeCN (*ca.* 10 ml) in a glass column (120 mm × 15 mm i.d.) with glass sinter and stopcock. After washing the resin with MeCN (*ca.* 50 ml), a solution of the compound to be oxidized (1–5 mg/ml) was percolated (1–5 ml/m) through the resin bed, all under N_2. The product was obtained by evaporation of the column effluent. In this manner, a sample of quinone resin (1 g, 0.73×10^{-3} moles of quinone) treated with trimethylhydroquinone (130 mg in 100 ml CH_3CN) produced trimethylbenzoquinone (0.72×10^{-3} moles) as determined by integration of the output of a Cecil effluent monitor set to the quinone absorption at 439 nm, plotted against the volume of effluent. The curve showed a steep rise between 8 and 13 ml, a flat plateau to 72 ml followed by a S-shaped descent completed at 92 ml after *ca.* 1 h.

(b) The same hydroquinone in a stirred solution containing suspended quinone resin beads was oxidized 50% (of the final value) in 90 min and 90% after *ca.* 5 H.

(c) To ensure rapid and complete preparative oxidations, a molar excess of quinone resin to hydroquinone was normally used. Such a column efficiently prepared methyl 1,4-naphthaquinone-2-carboxylate from the corresponding hydroquinone. Evaporation of the column effluent and sublimation (80°, 0.1 mm) gave yellow crystals, m.p. 86–87° (Found: C, 66.3; H, 3.7 $C_{12}H_{18}O_4$ requires C, 66.6; H, 3.7%). IR (mull) 1740, 1670 cm^{-1}: MS 218 (M$^+$, 22%) 216 (45), 186 (100), 158 (25), 157 (15), 130 (25), 129 (15), 101 (13), 102 (13).

Preparation and Analysis of Polymer-bound Cyanoquinones

4-(3',4'-Dicyano-2',5'-dihydroxyphenyl)butanoic acid. Hydro cyanation of the above quinonyl acid readily took place by the method of Wallenfels *et al.*[6] but the resulting mixture of hydroquinones could not be efficiently separated.

4-(2'-5'-Dihydroxyphenyl)butanoic acid (10 g) was refluxed in ethanol with benzyl chloride (7.1 g) and triethylamine (5.1 g) under N_2 for 24 h. The benzyl ester, NMR ($CDCl_3$) δ 1.96 (2H, q, 8 Hz), 2.44 (2H, t, 6 Hz), 2.63 (2H, t, 8 Hz), 5.14 (2H, s), 6.56 (3H, m), 7.3 (5H, br s), showed only one spot on tlc, but could not be crystallised. The oily ester (18 g) was sitrred with ceric ammonium nitrate (75 g) in 50% aqueous CH_3CN (150 ml) buffered with sodium acetate (47 g) for 0.5 h. Dilution and extraction yielded yellow crystals of benzyl 4-(2',5'-benzoquinonyl)-butanoate, m.p. 43.5–45° from hexane (Found: C, 71.8; H, 5.8. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.7%). NMR ($CDCl_3$) δ 1.94 (2H, q, 8 Hz), 2.4 (4H, m), 5.10 (2H, s), 6.50 (1H, br s), 6.70 (2H, s), 7.3 (5H, m); IR (mull) 1720, 1650 cm^{-1}; MS 286 (18%), 284 (M$^+$, 3), 178 (50), 123 (33), 92 (30), 91 (100).

The quinonyl ester in DMSO was treated with excess of liquid HCN in MeCN containing KCN (30 mg). After 1 h, no quinone remained. The reaction mixture was diluted, treated with sodium bicarbonate to give pH 8. After extraction with ether the aqueous layer was acidified to pH 1, stirred for 2 h and extracted with ether. This yielded 4-(3,4-dicyano-2',5'-dihydroxyphenyl) butanoic acid as a tan powder, m.p. 193° which could not be recrystallized but was purified by trituration with cold ether (Found: C, 58.6; H, 4.3; N, 11.0. $C_{12}H_{10}N_4O_4$ requires C, 58.5; H, 4.1; N, 11.3%). NMR (C_3D_6O) δ1.84–1.77 (2H, m), 2.38 (2H, t, 8 Hz), 2.74 (2H, t, 8 Hz), 7.18 (1H, s); IR (mull) 3425, 3100, 2255, 1700, 1620, 1600 cm^{-1}; MS 246 (M$^+$, 46%), 228 (100), 200 (23), 186 (23), 185 (58), 128 (23), 117 (27), 104 (19), 90 (31).

Hydrocyanation of quinone resin (2). The quinone resin (1 g) was suspended in dry DMSO (10 ml) and stirred for 10 min under nitrogen. Hydrogen cyanide (1 ml) in MeCN (2 ml) was added and stirred in for 10 min after which KCN (8 mg) was added and the whole stirred for 12 h. Filtration and washing gave the cyanated resin as dark brown beads (Found: C, 81.5; H, 7.5; N, 2.0; O, 6.3; Cl, 0.3%), IR (KCl) 3400, 2175, 1720, 1650 cm^{-1}.

Analysis of hydrocyanated resins by redox equilibrium. Equilibria were determined by suspending the resin (*ca.* 1 g) in CH_3CN (*ca.* 10 ml), adding a solution of the test quinone or hydroquinone (*ca.* 50–90 mg) in MeCN (*ca.* 10 ml) and stirring under nitrogen for several hours. Aliquots (2 ml) of the supernatant solution were taken at intervals and titrated for quinone by the method of Valeur[17] which gave ±2% with standard samples.

Products of Hydrocyanation of benzoquinone

2,3-Dicyanohydroquinone (5). Benzoquinone was treated either by the method of Wallenfels *et al.*[6] or with HCN/KCN in CH_3CN or DMSO as follows. Benzoquinone (700 mg) and KCN (20 mg) were dissolved in MeCN (40 ml) and a molar excess of HCN in CH_3CN was added dropwise with stirring. When the benzoquinone had been consumed (tlc; Merck silica gel 60, $Et_2O/CHCl_3$) the product was recovered in the usual way[6] as light brown crystals (yield 80% after recrystallization from aqueous EtOH), m.p. 230° (lit[6] 230°). NMR ($CDCl_3$) δ7.12 (s).

Identification of monocyanohydroquinone (6). (a) Analysis of the crude reaction products from various preparations by hplc (Bondapak/C_{18}, MeOH/acetate buffer) showed a peak of identical retention time to that of authentic 2, 5-dihydroxyphenylcyanide in up to 4% yield. (b) Benzoquinone was hydrocyanated by the method of Wallenfels *et al.*[6] and on cooling, 2, 3-dicyano-hydroquinone crystallized out of the reaction mixture. The mother liquors were evaporated and the residue treated with excess CH_2N_2/BF_3 in Et_2O. Extraction with aqueous alkali removed (unmethylated) hydroquinone. The ether layer was evaporated and the residue chromatographed (Merck silica gel 60, hexane/EtOAc 10%) to yield 2.5% of recrystallized 2, 5-dimethoxyphenyl cyanide, m.p. 170–173° (lit[7] 169–173°) which was identical to authentic material by mixed m.p., glc, tlc and IR. (c) Glc analysis of the methylated (CH_2N_2) hydrocyanation reaction products showed peaks of retention time identical to that of authentic 2, 5-dimethoxyphenyl cyanide on four stationary phases (SE30, FFAP, B34/DEGS and XF1150).

2, 3-Dicyanocyclohexa-1, 3-diene-1, 4-diol (15). 2, 3-Dicyano-

hydroquinone was reduced with sodium amalgam in aqueous alkali as described previously.[11] The product was recrystallized from EtOH/hexane at −20° to give the diol as colourless crystals which yellowed at 155° and turned to a red oil at 164–170° (lit.[11] 160–170°) (Found: C, 58.9; H, 3.8; N, 16.9. Calc. for $C_8H_6N_2O_2$. C, 59.2; H, 3.8; N, 17.2%). NMR ($CDCl_3$) δ 2.54 (s); IR (mull) 3125, 2225, 1635, 1295, 1275, 940, 720 cm^{-1}; UV (EtOH), 213 (log ϵ4.15), 235 (3.83), 260 (3.81), 268 (3.78), 339 (3.58); (MS 162 (M^+, 100%), 160 (30), 135 (26), 120 (30), 106 (35), 92 (32), 74 (42). The diol was refluxed with acetic anhydride and NaOAc for 0.5 h, the mixture diluted with water and the precipitate recrystallized from benzene/hexane to give the diacetate as colourless crystals, m.p. 162.5–164° (Found: C, 58.7; H, 3.9; N, 11.2. $C_{12}H_{10}N_2O_4$ requires C, 58.5; H, 4.1, N, 11.4%). NMR ($CDCl_3$) δ2.30 (6H, s), 2.54 (4H, s); MS 246 (M^+, 10%), 245 (10), 244 (47), 204 (23), 202 (72), 160 (100).

2,3-*Dicyanocyclohex-2-ene*1,4-*dione* (**16**). A solution of (**15**) treated with equimolar benzoquinone or nitrogen oxides gave a yellow solution of dione (**16**). NMR ($CDCl_3$) δ 3.10. This spectrum slowly gave place to that of 2, 3-dicyano-1, 4-hydroquinone. Attempts to isolate the dione yielded only the latter.

Cyclopentadiene adducts of (**16**) *and* 2,3-*dicyanobenzoquinone*. A solution of (**16**) treated with cyclopentadiene in MeOH yielded an immediate precipitate with loss of the yellow colour. Recrystallization of the precipitate from EtOAc/hexane gave colourless crystals of adduct (**17**) of double m.p. 149–150° and 260° (Found: C, 68.9; H, 4.7; N, 12.2. $C_{13}H_{10}N_2O_2$ requires C, 69.1, H, 4.4, N, 12.4%). NMR ($CDCl_3$) δ 2.06 (2H, ABq, $\Delta\nu$24 Hz, J_{AB} = 10 Hz), 2.60 (2H, m), 3.10 (2H, m), 3.92 (2H, br d, J = 1 Hz), 6.32 (2H, br s); IR (mull) 2240, 1715–1700, 1670, 1415 cm^{-1}; MS 226 (M^+, 12%), 197 (9), 184 (16), 161 (11), 105 (10), 66 (100).

2, 3-Dicyano-1, 4-benzoquinone (500 mg) in methanol (15 ml) treated with cyclopentadiene (0.15 ml) gave an immediate precipitate (560 mg). Recrystallization from EtOAc/hexane gave colourless crystals of adduct (18) of double m.p. 135–136° and 256° (Found: C, 69.7; H, 3.8; N, 12.4. $C_{13}H_8N_2O_2$ requires C, 69.6; H, 3.6; N, 12.5%). NMR ($CDCl_3$) δ2.16 (2H, ABq, $\Delta\nu$ 25 Hz, J_{AB} = 12 Hz), 4.0 (2H, d, 1 Hz), 6.24 (2H, br s), 6.84 (2H, s); IR (mull) 2245, 1680, 1600, 1590 cm^{-1}.

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