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Synthesis and Interconversion by Hydrogen Exchange of Isomeric Quinhydrones[1,2]

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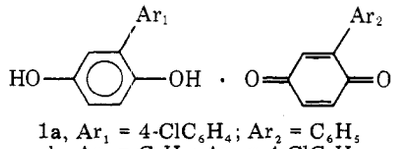
Isomeric quinhydrones, 2-phenylquinone/2-(4′-chlorophenyl)hydroquinone (1:1) (**1a**) and 2-(4′-chlorophenyl)-quinone/2-phenylhydroquinone (1:1) (**1b**), have been prepared as crystalline solids and shown to resist interconversion by a redox (hydrogen exchange) process even at temperatures as high as 140 °C when kept in the solid state. It is suggested that these unsymmetrically substituted complexes are inert to oxidation–reduction interconversions because of a stabilizing combination of hydrogen bonding and charge-transfer forces. A semiquantitative survey of the rates in solution of the redox equilibration of a number of quinone–hydroquinone pairs has been studied by NMR spectroscopy as the basis for the rational selection of the pair of quinhydrones described above.

Molecular complexes (1:1) (quinhydrones) of benzoquinones and hydroquinones have long been known as stable solids which, however, in solution separate into their components.[3] The possibility of preparing isomeric quinhydrones by virtue of the presence of different substituents on the quinone and hydroquinone ring has been recognized, and investigations of deuterium- and carbon-14-labeled compounds have been carried out as a method of studying the redox interconversions in solution of such compounds.[4] In other cases where preparation of isomeric pairs of substituted quinhydrones has been attempted, the rapid redox interconversion in solution coupled with a lack of adequate methods of characterization has led to confusing results.[5] Nevertheless crystals of unsymmetrically substituted complexes of this type as, for example, **1a** and **1b**, could be of great interest, because of their possible optical and electrical properties coupled with the fact that their interconversion requires only the transfer between oxygen atoms of hydrogen atoms (or hydride ions plus protons). Furthermore, determinations of the crystal structures of the monoclinic[6a] and triclinic[6b] forms of the parent symmetrical quinhydrone (1 with $Ar_1 = Ar_2 = H$) have shown that in each case the structures are composed of chains of alternating, well-defined, quinone and hydroquinone molecules hydrogen bonded in such a way that it might be hoped that hydrogen switching could be induced without seriously disrupting the structure.[7] With the proper choice of substituents, spectral or other properties should differ sufficiently for the isomers analogous to **1a** and **1b** to permit ready recognition of whether a crystal is in state **1a** or state **1b**.



1a, Ar_1 = 4-ClC_6H_4; Ar_2 = C_6H_5
b, Ar_1 = C_6H_5; Ar_2 = 4-ClC_6H_4
c, $Ar_1 = Ar_2 = C_6H_5$
d, $Ar_1 = Ar_2$ = 4-ClC_6H_4

This paper describes a study of the factors affecting the redox interconversion of hydroquinone–quinone pairs in solution and the synthesis of the crystalline redox isomers **1a** and **1b**.

Experimental Section

Spectra and other supplementary experimental data are available in ref 1.

Synthesis of Quinones and Hydroquinones. Hydroquinone-*2,3,5,6-d*$_4$. To 40 mL of acetyl chloride was added, over 30–45 min, 20 mL of D_2O (90% D, Columbia Organic Chemicals) with regular stirring and such that the evolution of gas was not too vigorous. The hydrolyzed mixture was added to 2.1 g of hydroquinone (Mallinckrodt, twice sublimed, mp 171 °C) and 4.0 g of amalgamated zinc and the resulting mixture was heated under reflux for 24 h.[8] The reaction was arrested with about 150 mL of water and the reaction mixture was repeatedly extracted with ether. The combined ethereal extracts were washed with $NaHCO_3$ solution until the washings remained alkaline. The organic layer was dried and the ether was removed to leave the crude deuterated hydroquinone which was sublimed at 70 °C and at 0.04 Torr to give 1.75 g (82%) of product that showed approximately 88% deuterium incorporation (by NMR and mass spectrometry). A final recrystallization from ethanol–benzene yielded 1.42 g (68%) of solid: mp 171–173 °C (lit. mp 175 °C);[9] IR (KBr) 3270, 2234, and 1210 cm^{-1}; mass spectrum (CH-5, 10 eV) M^+ (base peak) (*m/e*) 114, 113 (39%), 112 (22%).

Anal. Calcd for $C_6D_4(OH)_2$ with 88% D: C, 63.44; H, 5.29. Found: C, 63.08; H, 5.53.

2,5-Dichlorohydroquinone-*3,6-d*$_2$. 2,5-Dichloro-1,4-benzoquinone was reduced to the hydroquinone with $SnCl_2$ in virtually quantitative yield.[10,11] This hydroquinone (250 mg) was deuterated

in the manner described above. After two exchanges the partially deuterated compound (185 mg) was sublimed at 70 °C and 0.04 Torr to yield 161 mg (64%) of 2,5-dichlorohydroquinone containing 80% D in the aromatic positions as shown by NMR (82% by mass spectrometry): mp 171–172 °C (lit. mp 172 °C);[12] IR (KBr) 3390, 2286, 1205, and 1190 cm^{-1}; mass spectrum (CH-5, 10 eV) M^+ (*m/e*) 180, 184, base peak 180, 179 (29%), 181 (29%), 182 (64%), 183 (7%), 184 (11%).

Anal. Calcd for $C_6D_2Cl_2(OH)_2$ with 82% D: C, 39.95; H, 1.34; Cl, 39.33. Found: C, 39.78, H, 1.56; Cl, 39.27.

2,5-Di-*tert*-Butylhydroquinone-*3,6-d*$_2$. The unlabeled hydroquinone (0.5 g) was deuterated as above. Recrystallization from 1:1 ethanol–water and sublimation at 100 °C and 0.04 Torr gave 0.30 g (60%) of the deuterated compound. The IR spectrum showed no O–D stretching vibrations and the intensity of the hydroxylic proton singlet was used as an internal reference in the ^1H NMR experiments to obtain the percent D in the aromatic positions since the methyl groups were also deuterated extensively: mp 213 °C (lit. mp 213 °C);[13] IR (KBr) 3420, 2940, 2220, and 2140 cm^{-1}; NMR (acetone-d_6) δ 7.3 (s, 2 H, hydroxyl), 6.7 (s, 2 H, aromatic shows 82% deuterium), 1.35 (s, 18 H, aliphatic shows 73% D); mass spectrum (CH-5, 10 eV) M^+ at *m/e* 242, base peak 240, 238 (71%), 239 (84%), 241 (91%), 244 (21%).

Methylhydroquinone-*3,5,6-d*$_3$. The unlabeled methylhydroquinone (0.5 g) was deuterated as above. The crude material was sublimed at 60 °C and 0.04 Torr to yield 0.47 g (94%) of solid: mp 124–127 °C (lit. mp 127 °C);[14] IR (KBr) 3350, 1400, 1160, and 1040 cm^{-1}; ^1H NMR shows that deuterium incorporation is almost 100%.

Anal. Calcd for $C_7D_3H_5O_2$: C, 66.14; H, 6.30. Found: C, 66.13; H, 6.50.

Purification of 1,4-Naphthoquinone. The crude black powder purchased from the Aldrich Chemical Co. was recrystallized from AcOH–water to yield a brown solid. Recrystallization from an ethanolic solution containing animal charcoal followed by sublimation at 50 °C and 0.04 Torr gave light yellow crystals, mp 126 °C.

2-Phenyl-1,4-benzoquinone was prepared by the method of Brassard and L'Écuyer.[15] The diazonium salt of aniline was allowed to react with quinone (Eastman, twice sublimed). The reaction time was, however, increased to 36 h since insufficient product was obtained in the prescribed time.[15] The crude solid was recrystallized from high boiling petroleum ether and sublimed at 90 °C and 0.05 Torr to give the pure compound in 51% total yield: mp 110–112 °C (lit. mp 112 °C);[16] NMR ($CDCl_3$) δ 7.6 (s, 5 H), 6.9 (s, 3 H).

2-(4′-Chlorophenyl)-1,4-benzoquinone was obtained from the diazonium salt of *p*-chloroaniline by an analogous method.[15] Recrystallization from 2:1 EtOH–acetone followed by sublimation at 100 °C and 0.05 Torr gave the compound in 71% total yield: mp 129–130 °C (lit. mp 129 °C);[16] NMR (acetone-d_6) δ 7.5 (m, 4 H), 6.9 (s, 3 H).

2-Phenyl-1,4-dihydroxybenzene (2-Phenylhydroquinone). Although the other quinones used in this study were readily reduced, even when crude, to hydroquinones which were easily isolated as crystalline solids, on treatment with acidic $SnCl_2$,[10,11] phenylquinone did not readily give a solid product on reduction. Reduction itself seemed to occur easily as the color of the solution changed from yellow to colorless. Yet no solid could be induced to crystallize from solution. When the reduction was repeated on a large quantity (20 g) of analytically pure quinone, the reaction mixture separated into two layers. On cooling the mixture to 0 °C and scratching the sides of the vessel the hydroquinone crystallized slowly. Phenylhydroquinone was obtained from phenylquinone in essentially quantitative yield: mp 100 °C (lit. mp 97 °C);[17] ^1H NMR (DMSO-d_6) δ 8.6 (d, 2 H), 7.2–7.7 (m, 5 H), 6.5–7.1 (m, 3 H).

2-(4′-Chlorophenyl)-1,4-dihydroxybenzene (2-(4′-Chlorophenyl)hydroquinone). Reduction of the 4-chlorophenylquinone (20 g) with $SnCl_2$ in acidic EtOH–water gave 20.1 g (99.6%) of hydroquinone.[18] In this and the previous reduction, quinone of a high purity seems to be required if the hydroquinone is to crystallize easily. Sublimation at 110 °C and 0.05 Torr gave a white solid: mp 118–120 °C; NMR (DMSO-d_6) δ 8.8 (s, 2 H), 7.5 (q, 4 H), 6.7 (m, 3 H).

Anal. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.08; Cl, 16.10. Found: C, 65.60; H, 4.17; Cl, 15.99.

Equilibration Experiments. The NMR studies were carried out by weighing out equivalent amounts of the analytically pure quinone and hydroquinone under study, adding a previously calculated volume of solvent (deuterated when necessary), and recording the NMR spectra immediately. Additional spectra were recorded at suitable time intervals, depending on the reaction rate. Spectra were measured at a probe temperature of 44 °C. Integration of the NMR peaks was performed with a Keuffel and Esser planimeter. Details of the procedure and calculations employed are illustrated for one set of compounds.

Oxidation–Reduction Reaction between 1,4-Naphthoquinone and Tetramethyl-1,4-dihydroxybenzene. Naphthoquinone (19.8 mg) and the tetramethylhydroquinone (20.8 mg) were dissolved in 0.5 mL of DMSO-d_6. The methyl resonance of the tetramethylhydroquinone (124 Hz) decreases in intensity and the methyl resonance of tetramethylquinone (116 Hz) increases in intensity as the reaction goes toward equilibrium. Integration of the relative intensities of these peaks gives a measure of the extent of equilibration.

The initial concentrations of the species are A_0, B_0, C_0, and D_0 and the concentrations of the species at time t are A_t, B_t, C_t, and D_t. If $C_0 = D_0 = 0$ and $A_0 = B_0$, then $A_t = A_0 - x$ and $B_t = A_0 - x$, and $C_t = D_t = x$, where x is the number of moles/liter the starting materials lost or products gained at time t. Now for the above reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D, \quad \text{where } K = \frac{k_1}{k_{-1}} \neq 1$$

$$\frac{dx}{dt} = k_1(A_0 - x)(A_0 - x) - k_{-1}x^2$$

On integration we obtain:

$$\ln \frac{A_0(K^{1/2}+1) - x(1 - [1/K])K^{1/2}}{A_0(K^{1/2}-1) - x(1 - [1/K])K^{1/2}} = \frac{2ak_1t}{K^{1/2}} + \ln \frac{K^{1/2}+1}{K^{1/2}-1}$$

$$\log \frac{A_0(K^{1/2}+1) - x(1 - [1/K])K^{1/2}}{A_0(K^{1/2}-1) - x(1 - [1/K])K^{1/2}} = \frac{2ak_1t}{2.303K^{1/2}} + \log \frac{K^{1/2}+1}{K^{1/2}-1}$$

i.e., $\log Z = \alpha t + c$, where α and c are constants. In this example $A_0 = 0.25$ and $K = 5.44$. The value of K was calculated from the position of equilibrium. A plot of $\log Z$ vs. t gave a straight line with a positive slope and intercept. Eighteen points were included and the standard deviation in the slope was about 3%. Simple substitution in the rate equation gave a value for the time required for a 90% (or any other desired percentage) exchange.

Equilibration of Quinones and Their Hydroquinones Obtained by Reduction. Three quinones, *p*-benzoquinone, 2,5-dichloro-1,4-benzoquinone, and 2,5-di-*tert*-butyl-1,4-benzoquinone, were studied. In each case the hydroquinone obtained from the quinone by reduction was deuterated as described and equivalent amounts of the quinone and deuterated hydroquinones were used. In these cases $K = 1$ and the second-order rate expression simplifies to

$$(1/p) \ln [p(A_0 - x) + q] = kt + c$$

where

$$p = -(A_0 + B_0), \quad q = A_0B_0$$

and k and c are constants.

A_0, B_0, and t have the same meaning as before. Thirteen points were included for benzoquinone, fifteen for 2,5-dichlorobenzoquinone, and twenty for 2,5-di-*tert*-butylbenzoquinone. See Table I for the results.

Equilibration of Quinones and Hydroquinones Bearing Different Substitution Patterns. The data were handled as in the case of the tetramethylhydroquinone–naphthoquinone equilibrium experiment. Benzoquinone and methylhydroquinone exchange too rapidly for the equilibrium to be followed by NMR. Chloranil and hydroquinone equilibrate at a convenient rate. Twenty spectra were included. It was possible to follow the equilibration of 2,5-diphenylquinone and 2,5-di-*tert*-butylhydroquinone in DMSO, but rapid precipitation of the 2,5-diphenylquinone–2,5-diphenylhydroquinone 1:1 complex occurred in benzene (see Table I).

Unsymmetrical 2-Phenylquinone/2-(4′-Chlorophenyl)-hydroquinone 1:1 Complex, 1a. The quinone (0.5 g) and hydroquinone (0.6 g) were saturated separately in 3:1 benzene/AcOH and the two solutions were mixed. There was an immediate black precipitate which was filtered off within 15 s of precipitation: mp 162–165 °C; IR (KBr) 1633, 1495, and 1455 cm^{-1}.

Anal. Calcd for $C_{24}H_{17}O_4Cl$: C, 71.20; H, 4.20; Cl, 8.78. Found: C, 71.26; H, 4.20; Cl, 8.50.

Unsymmetrical 2-(4′-Chlorophenyl)quinone/2-phenylhydroquinone 1:1 Complex, 1b. This was prepared from 0.6 g of the quinone and 0.5 g of the hydroquinone as described in the preparation of **1a**. The blue-black precipitate was quickly filtered: mp 162–164 °C; IR (KBr) 1629, 1490, 1455, and 1432 cm^{-1}.

Anal. Calcd for $C_{24}H_{17}O_4Cl$: C, 71.20; H, 4.20; Cl, 8.78. Found: C, 70.98; H, 4.20; Cl, 9.02.

Characterization of the Unsymmetrical Complexes 1a and 1b by NMR. The complexes were dissolved separately in DMSO-d_6 (30 mg in 0.5 mL). NMR spectra were recorded after about 5 min. Addi-

Table I. NMR Studies on the Equilibration of Quinone/Hydroquinone Pairs[a,j]

$$Q_1 + HQ_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Q_2 + HQ_2 \qquad K = k_1/k_{-1}$$

Starting quinone Q_1	Starting hydroquinone HQ_1	Registry no.	Initial concn of each, mol/L	Solvent	^{1}H NMR feature obsd[b] Reactants signal (decreases)	^{1}H NMR feature obsd[b] Product signal (increases)	% of Q_1 (= HQ_1) at equil (value of K)	Time required for 90% reaction, min[c,d]	Formation of complex (ref)
(1) *p*-Benzoquinone	Hydroquinone-*2,3,5,6-d*$_4$	63715-58-2	0.25	Acetone or DMSO	Q (4 H)	HQ (4 H)	50 (1)	12	Yes (*e*)
(2) 2,5-Dichloro-*p*-benzoquinone	2,5-Dichlorohydroquinone-*3,6-d*$_2$	63715-60-6	0.25	DMSO	Q (2 H)	HQ (2 H)	50 (1)	65	Yes (*f*)
(3) 2,5-Di-*tert*-butyl-*p*-benzoquinone	2,5-Di-*tert*-butylhydroquinone-*3,6-d*$_2$	63743-82-8	0.41	Acetone	Q (2 H)	HQ (2 H)	50 (1)	35	Yes (*g*)
(4) *p*-Benzoquinone	Methylhydroquinone-*3,5,6-d*$_3$	63715-62-8	0.25	Acetone	Q (4 H)	HQ (4 H)	19 (18.2)	0	?
(5) 1,4-Naphthoquinone	Tetramethylhydroquinone	63715-63-9	0.25	DMSO	HQ (12 H)	Q (12 H)	30 (5.4)	3060	No (*g*)
(6) Tetrachloro-*p*-benzoquinone	Hydroquinone	63715-64-0	0.25	DMSO	HQ (4 H)	Q (4 H)	62 (0.38)	77	No (*g*)
(7) 2,5-Diphenyl-*p*-benzoquinone	2,5-Di-*tert*-butylhydroquinone	63715-65-1	0.03	DMSO Benzene	HQ (18 H) HQ (18 H)	Q (18 H) Q (18 H)	5 (361) *i*	12[h] 3	No (*g*)
(8) 2-Phenyl-*p*-benzoquinone	2-(4′-Chlorophenyl)hydroquinone	63715-66-2	0.10	DMSO	m, δ 7.25–7.50 Hz (9 H)	s, 7.55 Hz (4 H)	71 (.17)	ca. 100	Yes (*g*)
(9) 2-(4′-Chlorophenyl)-*p*-benzoquinone	2-Phenylhydroquinone	63715-67-3	0.13	DMSO	s, δ 7.55 Hz (4 H)	m, δ 7.25–7.50	40 (2.25)	ca. 100	Yes (*g*)

[a] For details of a representative calculation, see Experimental Section. [b] Q = quinone, HQ = hydroquinone. [c] The maximum error in this value is ±18%. [d] This is the time required to reach 90% equilibrium concentration of products. [e] F. Wöhler, *Justus Liebigs Ann. Chem.*, **51**, 145 (1844). [f] A. R. Ling and J. L. Baker, *J. Chem. Soc.*, **63**, 1314 (1893). [g] This study. [h] When the equilibration was carried out in benzene, a precipitate of 2,5-diphenylquinhydrone was formed almost at once. The amount of precipitate obtained in 3 min showed that at least 36% exchange had occurred in that time; in comparison 36% exchange occurs in DMSO in 12 min and 90% exchange in DMSO in 40 min. Precipitation of the complex from DMSO does not occur under these conditions. [i] Precipitation of the complex occurs prior to equilibration. [j] NMR spectra of quinone/hydroquinone mixtures in solution were recorded at a probe temperature of 44 °C. Acetone and DMSO used for the spectra were fully deuterated.

tional spectra after various intervals of time were observed to change. After about 8 to 10 h the spectra showed no further change. Application of the second-order rate equation permits a calculation of extent of exchange at the time the "initial" NMR spectra (Figure 1) was run. The "final" spectra from complexes **1a** and **1b** give values of 71 and 60% of phenylquinone and chlorophenylhydroquinone at equilibrium. An average value of 65.5% leads to a value of K equal to 3.40. The kinetic parameters may be estimated from the observation that 90% equilibration is achieved in 100 min when **1b** is dissolved in DMSO-d_6. These parameters were used to calculate the amount of equilibration in 5 min.

1:1 Complex of 2-Phenylquinone and 2-Phenylhydroquinone, 1c. Solutions of the components saturated at 0 °C in 3:1 benzene/AcOH were mixed to give an immediate black precipitate which was filtered rapidly and dried: mp 178–180 °C (lit. mp 176 °C);[17-19] IR (KBr) 1629, 1490, 1455, and 1437 cm^{-1}. Single crystals were prepared by reaction of the components in a nonaqueous gel.[20] Optical goniometry showed the prominent face to be (001), interfacial angles observed (calcd): (001):(012) 55° (52.8°), (001):(012) 52° (52.8°), (001):(100) 77.7° (77.5°), (001):($\bar{1}$00) 103.5° (102.5°), (012):(100) 82.7° (82.5°), (0$\bar{1}$2):(100) 82.8° (82.5°).

Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.84; H, 4.86. Found: C, 78.04; H, 5.00.

1:1 Complex of 2-(4′-Chlorophenyl)quinone and 2-(4′-Chlorophenyl)hydroquinone, 1d. This complex was prepared by mixing saturated solutions of the components. It is a black solid: mp 168 °C; IR (KBr) 1640, 1495, and 1458 cm^{-1}.

Single crystals grown in a nonaqueous gel[20] were shown by optical goniometry to have as the prominent face (001), interfacial angles observed (calcd): (001):(100) 79.3° (79.7°), (001):($\bar{1}$00) 100.5° (100.3°), (001):(012) 57° (56.2°), (001):(02$\bar{1}$) 105° (99.4°), (001):(0$\bar{2}$1) 103.8° (99.4°), (100):(012) 85.8° (84.3°), (100):(02$\bar{1}$) 89.9° (91.7), ($\bar{1}$00):(012) 93.4° (95.7°), ($\bar{1}$00):(02$\bar{1}$) 90.3° (88.3°).

Anal. Calcd for $C_{24}H_{16}O_4Cl_2$: C, 65.60; H, 3.64; Cl, 16.17. Found: C, 65.66; H, 3.59; Cl, 16.20.

Attempts to Prepare Single Crystals of the Unsymmetrical Complexes 1a and 1b. Experiments using the constituent quinones and hydroquinones of these complexes in nonaqueous gels yielded only quinhydrone **1c** which was presumably formed after an initial redox reaction.[20]

Powder X-Ray Crystallographic Studies. Powder photographs were taken of samples of **1a, 1b, 1c,** and **1d** (Cu Kα radiation, Debye-Sherrer camera made by Charles Supper Co.) and powder diffractometer traces of all four samples were recorded by Dr. Ralph Pfeiffer and associates, Eli Lilly Co., Indianapolis, Ind. The values for the d spacings on the pictures from the symmetrical quinhydrones, **1c** and **1d,** could be correlated[21] with the known cell dimensions[22] for these complexes.[1] The positions of the powder lines on the photographs from **1a** and **1b** were identical, although the diffractometer traces did indicate some differences in intensities. Attempts to correlate the values for the observed d spacings for **1a** and **1b** with those obtained from the cell dimensions (a = 5.98, b = 7.52, c = 20.30 Å, β = 102.5°) for the symmetrical complex **1c** did not result in a good fit. A much better fit was found when the cell dimensions for **1d** (a = 5.98, b = 7.45, c = 22.92 Å, β = 100.34°) or those obtained (a = 5.98, b = 7.48, c = 21.61 Å, β = 101.42°) by averaging the cell dimensions for the symmetrical quinhydrones **1c** and **1d** were used in the comparison.

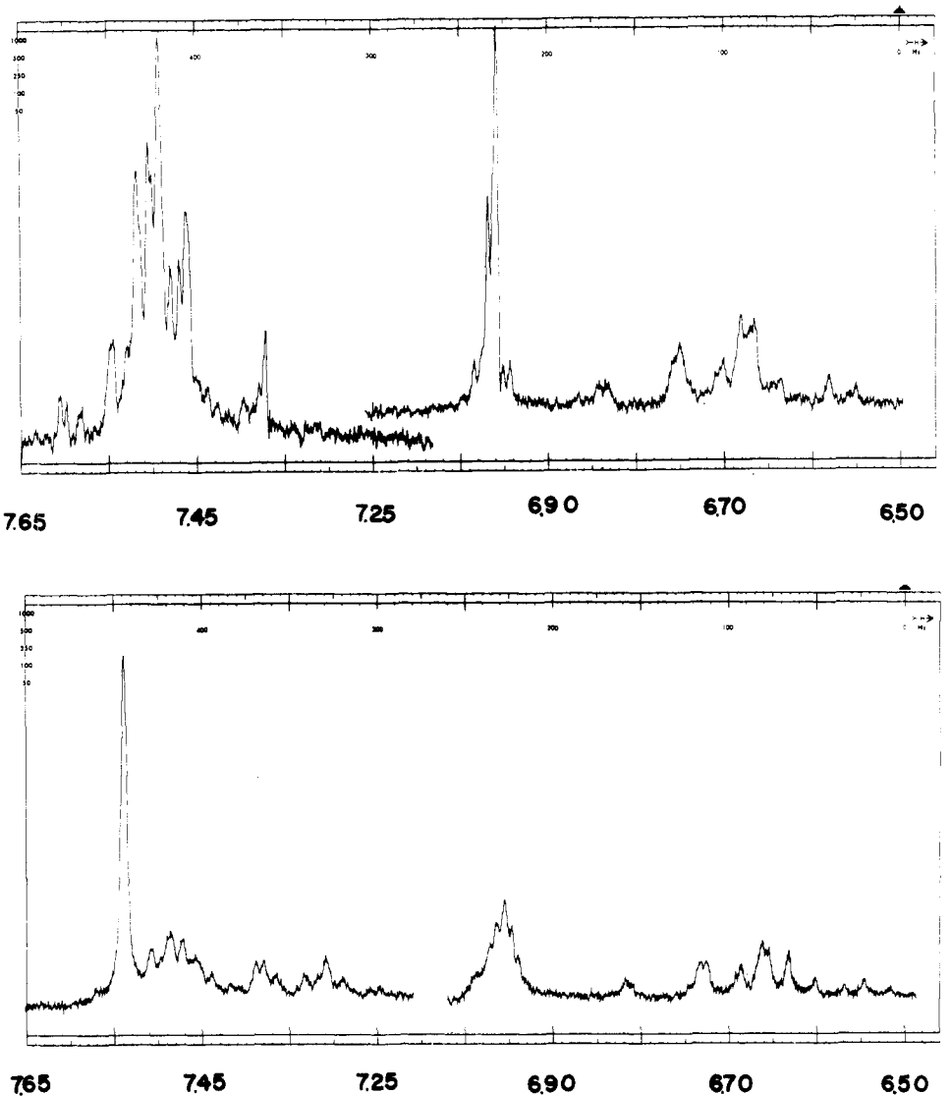


Figure 1. Upper: NMR spectrum of complex **1b** about 5 min after it was dissolved in DMSO. Shifts in ppm downfield from Me_4Si are shown at the bottom of the spectrum. Lower: NMR spectrum of complex **1a** about 5 min after it was dissolved in DMSO. Shifts in ppm downfield from Me_4Si are shown at the bottom of the spectrum.

Results and Discussion

The formation of a quinhydrone complex from a quinone and a hydroquinone bearing different substituents is complicated by the reversible redox reaction that the two components undergo in solution. If the composition of such a complex is to be unambiguous, the complementary hydroquinone and quinone should be prevented from forming in appreciable amounts prior to complex precipitation; this condition is obtained when the rate of the redox reaction is relatively slow.

In Table I are summarized results of an NMR study of the exchange reactions of a number of quinone/hydroquinone pairs. Although no attempt was made to carry out detailed quantitative studies of the effect of substituents on this hydrogen exchange, there may be inferred certain tentative generalizations which served as a guide in the search for an appropriate set of compounds for study. An earlier study[4e] had suggested that an increase in acidity of the hydroquinone component of the starting mixture leads to faster exchange. A number of other factors seem to be of equal importance. Comparison of the exchanges (2) and (3) with (1) in Table I suggests that substitution of both the starting materials leads to retardation of the exchange rate. On the other hand examples (5)–(7) show that too much substitution prevents the formation of the desired complex. In this connection it is instructive to note some of the factors governing the formation of symmetrically substituted quinhydrones. The donor capability of the hydroquinone, the acceptor strength of the quinone, and steric factors all seem to be of some importance. For example, it may be noted that tetrachlorohydroquinone and chloranil do not form a quinhydrone partly because the former is not a sufficiently strong donor. Recently, the importance of the above factors in quinhydrone formation has been discussed[23] and these factors would appear to be of obvious importance in the formation of unsymmetrically substituted quinhydrones also. The comparison of DMSO with benzene as solvent suggests that the strong hydrogen-bond acceptor, DMSO, leads to slower exchange. Comparison of examples (4) and (1) suggests that a slow exchange rate is favored by a close balance of redox potentials of the two component pairs.

These considerations based on exchanges (1)–(7) in Table I led to the synthesis of the components of the exchanges in lines (8) and (9). As is seen in Table I this is a compromise between an adequately slow exchange rate on the one hand and sufficient reactivity for complex formation on the other.

Complexes **1a** and **1b** were formed rapidly (filtration in 30

s) when saturated solutions of the components in DMSO were mixed. The quinone/hydroquinone stoichiometry was 1:1 even when the relative concentrations of the components were varied widely. The infrared spectra (KBr disk) showed marked differences between 1400 and 1500 cm^{-1} but do not differ sufficiently to make it easy to set upper limits for possible small amounts of contamination of **1a** by **1b** and vice versa. The NMR spectrum of **1a** in DMSO (Figure 1) (measured after the complex had been dissolved for about 5 min) approximated the sum of the spectra of phenylquinone and 4′-chlorophenylhydroquinone. Similarly the spectrum of **1b** (Figure 1) was approximately the sum of the spectra of 4′-chlorophenylquinone and phenylhydroquinone. However, integration of spectral peaks indicated that the solution of **1a** measured after 5 min contained 17% of **1b** and that the solution of **1b** contained 15% of the components of **1a**. Since when the complex was prepared quinone and hydroquinone were in solution together for only about 30 s before the complex precipitated as compared with a time of 5 min (300 s) after dissolution for the spectral measurement, it seems clear that most of the equilibration occurred in each case when the complex was redissolved for spectral determination.[24]

The unsymmetrically substituted quinhydrones **1a** and **1b** in the crystalline state are stable indefinitely at ambient temperature; even when heated to 140 °C they do not undergo sufficient equilibration to be detected by infrared spectroscopy. The basis of this stability is suggested by the crystal structures of the monoclinic and triclinic forms of quinhydrone,[6] as well as the structure of the complex between 1,4-hydroquinone and 1,4-naphthoquinone,[25] and also the results[1] on the structures of the symmetrical compounds **1c** and **1d**. A common theme runs through all of these structures. Chains of alternating quinone and hydroquinine molecules held together by hydrogen bonding are formed. In turn, the chains associate by overlap of the π-electron systems of the hydroquinone and quinone rings in adjacent chains thus generating a two-dimensional layer of molecules. Any molecule in the layer is thus related to its neighbors by hydrogen bonding and by charge-transfer forces. Were the redox hydrogen exchange to occur, a whole layer would have to undergo the exchange simultaneously if the stabilizing effect of these highly specific interactions is not to be lost.

Experiments designed to obtain single crystals of the unsymmetrically substituted complexes **1a** and **1b** by gel diffusion[20] produced only single crystals of the unchlorinated quinhydrone **1c** by a process which must have involved redox interaction of the reactants before crystallization occurred. Even attempts to bias the situation by allowing the phenylquinone to diffuse into a gel containing an excess of chlorophenylhydroquinone produced only crystals of the unchlorinated complex **1c**.

It is to be hoped that the foundation laid in the present paper will lead to control of the rates of the hydrogen exchange and crystallization processes so as to make possible the preparation of single crystals of isomeric substituent-labeled quinhydrones.

Registry No.—**1c**, 41758-38-7; **1d**, 63715-68-4; hydroquinone-*2,3,5,6-d*$_4$, 25294-85-3; hydroquinone, 123-31-9; 2,5-dichlorohydroquinone-*3,6-d*$_2$, 63715-59-3; 2,5-dichloro-1,4-benzoquinone, 615-93-0; 2,5-di-*tert*-butylhydroquinone-*3,6-d*$_2$, 63715-69-5; 2,5-di-*tert*-butylhydroquinone, 86-58-4; methylhydroquinone-*3,5,6-d*$_3$, 63715-61-7; methylhydroquinone, 95-71-6; 1,4-naphthoquinone, 130-15-4; 2-phenyl-1,4-benzoquinone, 363-03-1; 2-(4′-chlorophenyl)-1,4-benzoquinone, 20307-43-1; 2-phenylhydroquinone, 1079-21-6; 2-(4′-chlorophenyl)-1,4-dihydroxybenzene, 10551-37-8; 2,5-di-*tert*-butylhydroquinone, 88-58-4; *p*-benzoquinone, 106-51-4; tetrachloro-*p*-benzoquinone, 118-75-2; 2,5-diphenyl-*p*-benzoquinone, 844-51-9; tetramethylhydroquinone, 527-18-4.

References and Notes

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