Formation of Crystalline Complexes between Polymethylated Quinones and Hydroquinones

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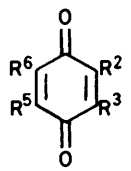
The effect of increased substitution by methyl groups on the formation of solid-state complexes of quinones with hydroquinones has been investigated. Both the ease and the stoicheiometry of complex formation of di-, tri-, and tetra-methylated quinones with hydroquinones, either by 'solid–solid' reaction or by recrystallization from a solvent, has been found to depend in part on the number of methyl substituents on each component. When there is methyl substitution on the hydroquinone moiety, a complex with components in 1 : 1 ratio is generally formed, while with methyl groups on the quinone molecule the ratio of quinone to hydroquinone in the complex is generally 1 : 2.

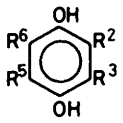
Furthermore the ease of complex formation can be highly structure-sensitive. Thus, although 1,4-benzoquinone reacts readily with 2,3,5,6-tetramethylhydroquinone to give a 2:1 complex, 2,3,5,6-tetramethylbenzoquinone and hydroquinone do not react when the two solids are ground together, crystallized from a solvent by the conventional procedure, or kept for long periods in contact with each other. Reaction of the two solids ground together can, however, be induced by heating the mixture at 80 °C; this is a convenient preparative method for the 1:1 product. Furthermore, seeding the solid mixture of the quinone and hydroquinone by addition of a small amount of the 1:1 product induces solid–solid reaction. Finally, a 1:2 complex of duroquinone with hydroquinone is formed when an ethyl acetate solution saturated with and containing an excess of each component suspended in the mixture is seeded with crystals of either the 1:1 or 1:2 complex. Similarly 2,5-dimethyl-1,4-benzoquinone can be induced to form both a 1:1 and a 2:1 complex with 2,5-dimethylhydroquinone.

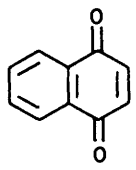
The reaction of quinones with hydroquinones to give deeply coloured crystalline 1:1 complexes (quinhydrones) has long been known[1] to occur readily in solution or even when the two solid reactants are ground together.[2,3] As the degree of substitution increases, reaction of the components may become more difficult. Thus, the doubly tetramethyl-substituted complex duroquinhydrone, from duroquinone (**13**) and durohydroquinone (**14**), was at first reported[4a] not to be formed by evaporation of the solvent from a solution of the components, although this complex was later prepared[4b,5] by suitably altering the solvent and procedure. Furthermore the complex of (**13**) with (**14**), although containing the components in 1:1 ratio, showed an OH stretching absorption in Fourier transform i.r. which was different from those of other previously prepared quinhydrones, and suggested an unusual type of hydrogen bonding.

Although the formation of complexes of quinones with hydroquinones in 1:1 ratio has been known for more than 90 years, no reports of other stoicheiometry appeared until 1982, when the structure of a 2:1 complex of 2,5-dimethyl-1,4-benzoquinone (**9**) with 2,5-dimethylhydroquinone (**10**) was reported.[2b] In a subsequent investigation of the reaction of the same quinone (**9**) with the unmethylated hydroquinone (**2**), there was obtained only a 1:2 complex, the crystal structure of which was reported.[2c]

This paper describes a further investigation into the effect of multiple methyl substitution on both the ease of complex formation and the stoicheiometry of complexes formed in the reactions of quinones with hydroquinones. The following paper[2e] reports the structures of complexes of duroquinone (**13**) with two hydroquinones (**1**) and (**14**), analyses the observed effects of methyl groups on stoicheiometry, and makes correlations of structure with the OH-stretching region of the Fourier transform i.r. spectrum.







(**19**)

(**1**)	(**2**)	$R^2 = R^3 = R^5 = R^6 = H$
(**3**)	(**4**)	$R^2 = Me, R^3 = R^5 = R^6 = H$
(**5**)	(**6**)	$R^2 = R^6 = Me, R^3 = R^5 = H$
(**7**)	(**8**)	$R^2 = R^3 = Me, R^5 = R^6 = H$
(**9**)	(**10**)	$R^2 = R^5 = Me, R^3 = R^6 = H$
(**11**)	(**12**)	$R^2 = R^3 = R^5 = Me, R^6 = H$
(**13**)	(**14**)	$R^2 = R^3 = R^5 = R^6 = Me$
(**15**)	(**16**)	$R^2 = Ph, R^3 = R^5 = R^6 = H$
(**17**)	(**18**)	$R^2 = p\text{-}ClC_6H_4, R^3 = R^5 = R^6 = H$

Experimental

Fourier transform i.r. (F.t.i.r.) spectra were obtained with a Nicolet 7000 Ftir spectrophotometer and differential calorimetry scans were recorded with a DuPont 900 Thermal Analyser.

Sources and Purification of the Quinones and Hydroquinones.—Information for 1,4-benzoquinone (**1**), 2-methyl-1,4-benzoquinone (**3**), 2,5-dimethyl-1,4-benzoquinone (**9**), 2-phenyl-1,4-benzoquinone (**15**), 2-(*p*-chlorophenyl)-1,4-benzoquinone (**17**), 1,4-naphthoquinone (**19**), and their corresponding hydroquinones has been given earlier.[2,6,7] 2,6-Dimethyl-1,4-benzoquinone (**5**), m.p. 72—73 °C, duroquinone (**13**), m.p. 111—112 °C, and 2,3,5-trimethylhydroquinone (**12**), m.p. 173—174 °C (Aldrich), were purified by sublimation. 2,3-Dimethyl-1,4-benzoquinone (**7**), m.p. 56—57 °C, was prepared[8] from 2,3-dimethylphenol and purified by steam distillation. 2,3-Dimethylhydroquinone (**8**), m.p. 223—224 °C, was prepared by reduction of 2,3-dimethylbenzoquinone (**7**) with aqueous sodium hydrogen sulphite[9] and purified by sublimation. 2,3,5-Trimethyl-1,4-benzoquinone (**11**), m.p. 30—31 °C, was obtained by oxidation of the hydroquinone

(**12**) by a method described earlier[10] for oxidation of hydroquinone (**2**). 2,6-Dimethylhydroquinone (**6**), m.p. 150—151 °C, was prepared by reduction of the quinone (**5**) with aqueous sodium hydrogen sulphite[9] and purified by sublimation. Durohydroquinone (**14**), m.p. 234—235 °C, prepared[11] from the quinone (**13**), was purified by crystallization from tetrahydrofuran or by sublimation.

1:1 *Complex of* 2,6-*Dimethyl*-1,4-*benzoquinone with* 2,6-*Dimethylhydroquinone* [(**5**)·(**6**)].—Equimolar amounts of the quinone (**5**) (272.3 mg, 2×10^{-3} mol) and hydroquinone (**6**) were dissolved in acetone (5 ml) and the solution was maintained at −20 °C for 24 h. The reddish-brown needles so obtained were filtered off to give the complex, m.p. 107—108 °C; F.t.i.r. (Nujol) ν 3 365 (sharp peak superimposed on broader triangular peak), 1 635s, and 1 610s cm^{-1}; δ_H[$(CD_3)_2SO$] 8.44 (s), 7.39 (s), 6.63 (s), 6.27 (s), 2.03 (s), and 1.94 (s); quinonoid:benzenoid H 0.96:1.00; quinone methyl:hydroquinone methyl 1.04:1.03 (theory for 1:1 complex 1.0). Differential scanning calorimetry (20 deg min^{-1}) showed a single sharp endotherm at 107 °C.

The same complex was obtained by grinding[2a] together the components in 1:1 ratio, as shown by comparison of F.t.i.r.

1:2 *Complex of* 2,6-*Dimethyl*-1,4-*benzoquinone with Hydroquinone* [(**5**)·(**2**)].—Attempts to prepare the 1:1 complex by crystallization[6] gave a blackish-red 1:2 complex, m.p. 121—122 °C; F.t.i.r. (Nujol) ν 3 380, 3 358, 3 170, 1 635s, and 1 618s cm^{-1} (absorptions at 3 260, 1 650, 1 423, 1 290, 1 190, 1 035, 1 007, 920, and 900 cm^{-1} disappeared during complex formation); δ_H[$(CD_3)_2SO$] 8.49 (s), 6.57 (s), 6.50 (s), and 1.94 (s), quinonoid/benzenoid H 0.44 (theory for 1:1 complex 0.5 and for 1:2 0.25). Grinding the quinone (**5**) (136.1 mg, 1×10^{-3} mol) with 2 equiv. of hydroquinone (**2**) gave a complex identical with that just described.

1:1 *Complex of* 1,4-*Benzoquinone with* 2,6-*Dimethylhydroquinone* [(**1**)·(**6**)].—When benzoquinone (**1**) (108.1 mg, 1×10^{-3} mol) was ground with an equivalent amount of 2,6-dimethylhydroquinone (**6**) (following an earlier procedure[2a]) there was obtained the black 1:1 complex, m.p. 97—98 °C; F.t.i.r. (Nujol) ν 3 358, 3 235, and 1 633s cm^{-1} (absorptions at 3 310, 1 658, 1 645, 1 347, 1 328, 1 235, and 1 072 cm^{-1} disappeared during grinding).

Attempted Preparation of a Complex of 2,3-*Dimethylbenzoquinone* (**7**) *with* 2,3-*Dimethylhydroquinone* (**8**).—When equimolar amounts of (**7**) (272.3 mg, 2×10^{-3} mol) and (**8**) were dissolved in acetone (5 ml), the solution became red but no complex precipitated even after 24 h at −20 °C. When equimolar amounts of (**7**) and (**8**) were ground together at room temperature (following an earlier procedure[2a]) the colour of the mixture became red but faded quickly due to sublimation of the quinone from the complex.

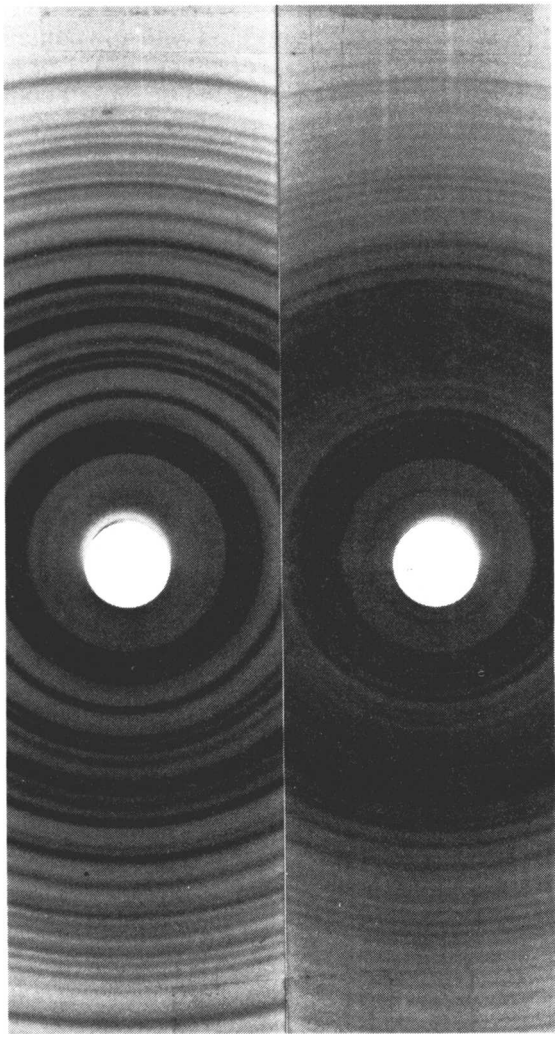
Preparation of the 1:1 *and* 2:1 *Complexes of* 2,5-*Dimethyl*-1,4-*benzoquinone* (**9**) *with* 2,5-*Dimethylhydroquinone* (**10**).—When a solution in ethyl acetate (50 ml) of equimolar amounts of the dimethylquinone (**9**) (272.3 mg, 2×10^{-3} mol) and the dimethylhydroquinone (**10**) was allowed to evaporate rapidly there was obtained a 1:1 complex, as bluish-red plates, δ_H [200 MHz; $(CD_3)_2SO$] 8.32 (s, 2 H), 6.72 (q, 2 H), 6.45 (s, 2 H), 1.99 (s, 6 H), and 1.95 (d, 6 H); F.t.i.r. (Nujol) ν 3 300, 1 663, and 1 628 cm^{-1}. The procedure (similar to this one) described in an earlier paper[2b] has now been found to produce preponderantly the 1:1 complex. The crystal chosen for the structure determination[2b] and shown to be a 2:1 complex was picked from a batch of crystals now known to consist mostly of the 1:1 complex.

The most reliable preparation of single crystals of the 2:1 complex is as follows. When a few microcrystals of the 2:1 (or even the 1:1) complex are added to a saturated solution in ethyl acetate of the dimethylquinone (**9**) and the dimethylhydroquinone (**10**) *containing suspended crystals of an excess of each of the reactants* (**9**) and (**10**) there were obtained within 24 h thick deep bluish-red crystals of the 2:1 complex, m.p. 117—118 °C; δ_H [360 MHz; $(CD_3)_2SO$] 8.32 (s, 2 H) 6.70 (q, 4 H, *J* 1.5 Hz), 6.43 (s, 2 H), 1.97 (s, 6 H), and 1.93 (d, 12 H, *J* 1.5 Hz); F.t.i.r. (Nujol) ν 3 390, 1 625, 1 540, 1 420, 1 205, 912, and 878 cm^{-1}.

The crystalline 1:1 and 2:1 complexes could be readily distinguished from each other by their F.t.i.r. spectra and also by their *X*-ray powder patterns (Figure).

The quinone (**9**) showed no visible solid–solid reaction with the hydroquinone (**10**) even after 2 months contact in a capillary tube, and no evidence of complex formation was obtained when the components were ground together at room temperature.

When crystals of (**9**) were ground with an equimolar amount of (**10**) and the mixture was heated in a capillary tube at 65 °C for 16 h it was converted into the bluish-red 2:1 complex already described, as shown by the appearance of F.t.i.r. peaks at 3 390, 1 625, 1 540, 1 420, 1 205, 912, and 878 cm^{-1}. The 2:1 stoicheiometry was confirmed by solution n.m.r. as already



X-ray powder diffraction patterns of (left) the 1:1 complex and (right) the 2:1 complex of the dimethylbenzoquinone (**9**) and the dimethylhydroquinone (**10**)

described. Similarly when the ground mixture of (**9**) and (**10**) was seeded with a crystal of the 2:1 complex it slowly yielded the 2:1 complex.

1:1 *Complex of* 2,3-*Dimethyl*-1,4-*benzoquinone with Hydroquinone* [(**7**)·(**2**)].—When equimolar amounts of (**7**) (272.3 mg, 2×10^{-3} mol) and (**2**) were dissolved in acetone (4 ml) and the solution was maintained at −20 °C for 24 h, there were obtained by filtration thick blackish-red plates of the complex, m.p. 109—110 °C; F.t.i.r. (Nujol) 3 360, 3 280, 1 630, and 1 620 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.61 (s), 6.81 (s), 6.53 (s), and 1.93 (s); quinonoid/aromatic H 0.5 (theory for 1:1 complex 0.5); F.t.i.r. absorptions at 3 220, 1 656, 1 240, 1 210, 1 005, 926, 913, 877, and 842 cm^{-1} disappeared during complex formation.

The same complex was obtained by grinding together a solid mixture of (**7**) and (**2**) as shown by F.t.i.r. comparison with the sample just described.

1:1 *Complex of* 1,4-*Benzoquinone with* 2,3-*Dimethylhydroquinone* [(**1**)·(**8**)].—When equimolar amounts of (**1**) (108.1 mg, 1×10^{-3} mol) and (**8**) were ground (following an earlier procedure[2a]) there was obtained a black 1:1 complex, m.p. 109—110 °C; F.t.i.r. (Nujol) ν 3 240 and 1 630 cm^{-1} (absorptions at 3 265, 1 658, 1 390, 1 307, 898, and 858 cm^{-1} disappeared during grinding).

1:1 *Complex of* 2,3,5-*Trimethyl*-1,4-*benzoquinone with* 2,3,5-*Trimethylhydroquinone* [(**11**)·(**12**)].—Equimolar amounts of the trimethylquinone (**11**) (300.4 mg, 2×10^{-3} mol) and the trimethylhydroquinone (**12**) were dissolved in acetone (1 ml). After addition of water (3 drops) the solution was maintained at −20 °C for 24 h. The blackish solid was filtered off to give the complex, m.p. 91—92 °C; F.t.i.r. (Nujol) ν 3 360 (sharp peak superimposed on broader triangular peak), 1 630, and 1 620 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.23 (s), 7.22 (s), 6.34 (s), and 1.9—2.1 (m), quinonoid/benzenoid H 1.0 (theory for 1:1 complex 1.0); differential scanning calorimetry (20 deg min^{-1}) showed a single sharp endotherm at 91 °C. The same complex was obtained by grinding[2a] together the components at 4 °C in 1:1 ratio, as shown by F.t.i.r. comparison.

1:2 *Complex of* 2,3,5-*Trimethyl*-1,4-*benzoquinone with Hydroquinone* [(**11**)·(**2**)].—Attempts to prepare the 1:1 complex from acetone gave a blackish-red complex, m.p. 91—92 °C; F.t.i.r. (Nujol) ν 3 390, 3 360, 3 185, 1 650, 1 628, and 1 617 cm^{-1} (absorptions at 3 260, 1 313, 1 260, 1 220, 1 190, and 1 185 cm^{-1} disappeared during reaction); $\delta_H[(CD_3)_2SO]$ 8.52 (s), 6.58 (m), 6.54 (s), and 1.85—2.0 (m), methyl/hydroxy H 3.25 (theory for 1:2, 2.25). The same complex was obtained by grinding together the components (**11**) and (**2**) in 1:2 ratio, as shown by F.t.i.r. comparison. F.t.i.r. of the sample prepared by grinding together the components in 1:1 ratio showed absorption due to the unchanged quinone together with that of the 1:2 complex.

1:1 *Complex of* 1,4-*Benzoquinone with* 2,3,5-*Trimethylhydroquinone* [(**1**)·(**12**)].—When benzoquinone (**1**) (108.1 mg, 1×10^{-3} mol) was ground with an equimolar amount of the hydroquinone (**12**) (following the earlier procedure[2a]) there was obtained the black 1:1 complex, m.p. 86—88 °C; F.t.i.r. (Nujol) ν 3 360, 3 230, and 1 631 cm^{-1} (absorptions at 3 300, 1 658, 1 645, 1 410, 1 365, 1 343, 1 310, 1 306, 900, 845, and 830 cm^{-1} disappeared during reaction).

1:1 *Complex of Duroquinone with Hydroquinone* [(**13**)·(**2**)].—When duroquinone (**13**) (164.2 mg, 1×10^{-3} mol) was ground with an equimolar amount of hydroquinone (**2**) and the mixture was heated at 80 °C for 2 h in an oil-bath there was obtained the red complex, m.p. 105—106 °C; F.t.i.r. (Nujol) ν 3 440 (s) and 1 627 cm^{-1} (absorptions at 3 260, 1 638, 1 306, 1 208, 1 190, 1 030, and 1 007 cm^{-1} disappeared during complex formation); differential scanning calorimetry showed a sharp endotherm at 107 °C. The complex could not be prepared by a conventional crystallization from solution. Thus when a mixture of the components in toluene–methanol (3:1) was held at −20 °C the only complex formed (after several weeks) was triclinic quinhydrone [(**1**)·(**2**)]. Attempts to carry out the solid–solid reaction at room temperature were unsuccessful. However, if the mixture of starting materials was nucleated with a few crystals of the product complex before grinding, complex formation occurred at room temperature, but very slowly.

1:2 *Complex of Duroquinone with Hydroquinone* [(**13**)·(**2**)].—To a solution in ethyl acetate, saturated with both duroquinone (**13**) and hydroquinone (**2**) and containing an excess of each component at the bottom of the container, were added a few microcrystals of the 1:1 complex. After 4 h there had formed thick deep red crystals of a 1:2 *complex* of (**13**) with (**2**), F.t.i.r. (Nujol) ν 3 405, 3 360, and 1 620 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 8.15 (s, 4 H), 6.33 (s, 8 H), and 1.90 (s, 12 H), $(CH_3)/(ArH)$ 1.56, 1.48 (theory for 1:2 complex, 1.50). Heating in a capillary tube caused sublimation of duroquinone (**13**) accompanied by partial melting at 110—112 °C and complete melting at 144—145 °C [Found: C, 68.8; H, 6.4. $C_{10}H_{12}O_2 \cdot 2(C_6H_6O_2)$ requires C, 68.7; H, 6.3%].

The same 1:2 complex was formed when these crystals of the 1:2 complex were used to seed a new crystallization. The crystal structure of this complex is reported in the following paper.[2e]

2:1 *Complex of* 1,4-*Benzoquinone with Durohydroquinone* [(**1**)·(**14**)].—Grinding the quinone (**1**) (216.2 mg, 2×10^{-3} mol) with durohydroquinone (**14**) (0.5 equiv.) gave the blackish-blue complex, m.p. 97—105 °C; F.t.i.r. (Nujol) ν 3 240 and 1 632 cm^{-1} (absorptions at 3 410, 1 658, 1 645, 1 420, 1 365, 1 240, 898, and 852 cm^{-1} disappeared during grinding.)

1:1 *Complex of Duroquinone with Durohydroquinone* [(**13**)·(**14**)].—This was prepared by the earlier procedure.[4b] Differential scanning calorimetry showed endotherms at 120 and 225 °C. When the sample was heated in capillary tube the red needles of the complex became yellowish-white with partial melting and sublimation of the quinone (112—115 °C) but with retention of the shapes of the crystals; melting was complete at 230—235 °C. Attempts to prepare the complex by grinding the components together even with seeding by the product complex or heating at 80 °C were unsuccessful.

Crystals of superior quality were obtained when a solution in acetone saturated with both duroquinone (**13**) and durohydroquinone (**14**) was seeded with a few microcrystals of the 1:1 complex already described. Large thick needles of the product had been formed after about 24 h. These crystals were employed in the crystal-structure determination reported in the following paper.[2e]

Spontaneous Decomposition of Quinhydrones.—Each of the quinone–hydroquinone complexes underwent decomposition with loss of the quinone. Thus the blackish-blue 1:1 complex of duroquinone (**13**) with durohydroquinone (**14**) became white within 24 h; the F.t.i.r. spectrum (Nujol) of the white residue was identical with that of the hydroquinone (**14**). Reddish-brown crystals of the 1:2 complex of methylbenzoquinone (**3**) with hydroquinone (**2**) became white in 72 h and the dark red 1:2 complex of duroquinone (**13**) with hydroquinone (**2**) became white in 1 000 h (42 days); in each of these cases the product was shown by F.t.i.r. (Nujol) and *X*-ray powder photography to be the β-form of hydroquinone (**2**) rather than the more stable α-form. Bluish-black crystals of the triclinic

form of the unsubstituted complex of the quinone (**1**) with hydroquinone (**2**) had decomposed in 2 200 h (3 months) to powder identified by F.t.i.r. and *X*-ray powder photographs as α-hydroquinone [α-(**2**)].

Rearrangement of Benzoquinone–2,6-Dimethylhydroquinone [(**1**)·(**6**)] *to the* 1:2 *Complex, 2,6-Dimethylbenzoquinone–Hydroquinone* [(**5**)·(**2**)].—When the black 1:1 complex of the quinone (**1**) with the hydroquinone (**6**) prepared by solid–solid reaction[2a] was heated in a capillary tube at 70 °C for 14 h or even when kept for 15 days at room temperature, the colour changed to reddish-brown. F.t.i.r. peaks at 3 235, 1 587, 1 300, 1 260, 1 194, 1 150, 947, 875, and 855 cm^{-1} had disappeared while others at 3 280, 3 170, 1 618, 1 355, 1 207, and 1 041 cm^{-1} appeared. The F.t.i.r. spectrum of the product was similar to that of the complex [(**5**)·(**2**)] prepared by crystallization of a mixture of (**5**) and (**2**) from solution. However, absorptions characteristic of the quinone (**5**), which should have been formed as a by-product of this reaction, were absent. It seems likely that the quinone (**5**) escaped by evaporation from the reacting crystals as it was formed. Differential scanning calorimetry (20 deg min^{-1}) of the starting complex [(**1**)·(**6**)] showed a small broad exotherm at 50—70 °C followed by endotherms at 87 °C and at 118 °C attributed to the melting of the dimethylquinone (**5**) (m.p. 72—73 °C) and the 1:2 complex, dimethylbenzoquinone–hydroquinone (**5**)·(**2**) (m.p. 121—122 °C). The latter complex, when prepared by crystallization from a solvent, showed a sharp endotherm at 122 °C.

Rearrangement of Benzoquinone–2,3-Dimethylhydroquinone [(**1**)·(**8**)] *to the* 1:1 *Complex, 2,3-Dimethylbenzoquinone–Hydroquinone* [(**7**)·(**2**)].—When the black 1:1 complex (**1**)·(**8**) prepared by a solid–solid reaction[2a] was heated in a capillary tube at 70 °C for 4 h or even when kept for 11 days at ambient temperature, the colour changed to reddish-brown. F.t.i.r. peaks at 3 240, 1 240, 1 075, 946, 870, 800, and 742 cm^{-1} had disappeared while others at 3 360, 3 280, 1 345, 1 138, 1 095, 1 062, and 810 cm^{-1} had appeared. The F.t.i.r. spectrum of the product was similar to that of the complex prepared by crystallization of a mixture of (**7**) and (**2**) as already described.

Rearrangement of Benzoquinone–2,3,5-Trimethylhydroquinone [(**1**)·(**12**)] *to the* 1:2 *Complex, 2,3,5-Trimethyl-1,4-Benzoquinone–Hydroquinone* [(**11**)·(**2**)].—When the black 1:1 complex of the quinone (**1**) with the trimethylhydroquinone (**12**) prepared by solid–solid reaction[2a] was heated in a capillary tube at 70 °C for 5 h, or even when kept for 10 days at room temperature, the colour changed to reddish-brown. F.t.i.r. peaks at 3 230, 1 631, 1 320, 1 285, 1 215, 1 080, 870, and 850 cm^{-1} had disappeared while others at 3 390, 3 190, 1 626, 1 618, 1 518, 1 350, 1 205, and 885 cm^{-1} had appeared. The F.t.i.r. spectrum of the product was similar to that of the complex of the trimethylquinone (**11**) with hydroquinone (**2**) prepared by crystallization from solution. However there was a small peak in the product at 1 650 cm^{-1} characteristic of the trimethylquinone (**11**), expected to have formed in this reaction. Differential scanning calorimetry (10 deg min^{-1}) of the complex showed a small endotherm at 50 °C and a large endotherm at 86 °C attributed to the melting of the trimethylquinone (**11**) and the 1:2 complex of (**11**) with hydroquinone (**2**) (m.p. 91—92 °C). When prepared by crystallization from a solvent the complex showed a sharp endotherm at 92 °C.

Rearrangement of the 2:1 *Complex, Benzoquinone–Durohydroquinone* [(**1**)·(**14**) *to the* 1:1 *Complex, Duroquinone–Hydroquinone* [(**13**)·(**2**)].—When the blackish-blue 2:1 complex prepared by solid–solid reaction was heated in a capillary tube at 60 °C for 6 h (or even when kept for 2 months at room temperature) the colour changed to red. F.t.i.r. (Nujol) peaks at 1 632, 1 305, and 1 100 cm^{-1} disappeared while new peaks appeared at 3 440, 1 627, 1 520, 1 348, 1 250, 1 200, and 1 126 cm^{-1}. Other peaks at 3 240, 1 480, 1 365, 1 220, and 950 cm^{-1} diminished in intensity but did not disappear entirely. When the sample was heated to 70 °C there was partial melting.

When an equimolar mixture of the blackish-blue 2:1 complex benzoquinone–durohydroquinone (**1**)·(**14**) with durohydroquinone (**14**) was heated at 80 °C for 6 h the colour changed to red. The F.t.i.r. spectrum after heating was identical with that of the 1:1 complex of duroquinone (**13**) with hydroquinone (**2**). The reaction was also found to go to completion without any sign of melting when carried out at 90 °C (2 h) or even at 100 °C (0.5 h). Differential scanning calorimetry (20 deg min^{-1}) of the 2:1 complex of the quinone (**1**) with durohydroquinone (**14**) showed a small broad exotherm at 50—70 °C followed by an endotherm attributed to melting of the complex of duroquinone (**13**) with hydroquinone (**2**) (m.p. 98 °C). The 1:1 complex prepared by heating equimolar amounts of (**13**) and (**2**) together showed a sharp endotherm at 107 °C.

Results and Discussion

Effect of Multiple Substitution on Quinhydrone Formation.—We have extended the investigation of the effect of multiple methyl substitution to complex formation from quinones and hydroquinones with 2,3- and 2,6-dimethyl and 2,3,5-trimethyl substituents. A new method of carrying out complex formation from a solution kept in contact with both solid components during crystallization gave, in a number of cases, larger and more perfect crystals of the complex and in some cases led to a complex not obtainable by other methods. An additional finding has been that certain solid–solid reactions which fail to occur at an appreciable rate at room temperature can be made to occur at a practical rate by heating the mixed solids to 80 °C.

A summary of the reactions of methylated quinones and hydroquinones is presented in the Table.

Stoicheiometry of Complex Formation.—The Table shows that substitution of methyl groups on the hydroquinone unit only (indicated by 'U' in the Table) leads in general to a quinhydrone complex with the 1:1 ratio of quinone to hydroquinone, the only exception being the benzoquinone–2,3,5,6-tetramethylhydroquinone complex formed with a ratio of 2:1. Those complexes in which the quinone and hydroquinone partner are identically substituted (indicated by 'Sym' in the Table) also form 1:1 complexes, with the single exception of the 2,5-dimethylquinone–2,5-dimethylhydroquinone complex which, in addition to the 1:1 complex, forms a complex with a quinone–hydroquinone ratio of 2:1.[2b] On the other hand, substitution of methyl groups on the quinone ring only (the 'S' isomers) leads in five of the seven cases in the Table to a complex with quinone and hydroquinone in the ratio of 1:2; the exceptions are complex formation of tetramethylquinone (**13**) with hydroquinone (**2**) where both a 1:1 and a 1:2 complex can be prepared, and the complex of the 2,3-dimethylquinone (**7**) with hydroquinone (**2**) where the ratio is 1:1. Although a structure determination of only one of the four 1:2 complexes in the Table has been previously published,[2c] a second such structure is reported in the following paper[2e] and some of the reasons for the unusual stoicheiometry will be discussed there.

Ease of Quinhydrone Formation and the Importance of Nucleation.—Clearly the presence of methyl groups on the quinone or hydroquinone ring can have a profound effect on the ease of complex formation, but an effect which is not readily predicted. For example, substitution of two methyl groups in

Table. Effect of multiple substitution on quinhydrone formation

Complex	Positions of methyl groups: Quinone	Positions of methyl groups: Hydroquinone	Method of synthesis[a]	Stability[b]	Composition ratio (Q:H)	Ref.
(1)-(2)	0	0	Sn, SS	Sym	1:1	12*a*, *c*
(3)-(2)	2	0	Sn, SS	S	1:2[c]	2*a*
(1)-(4)	0	2	SS	U	1:1	2*a*
(3)-(4)	2	2	Sn, SS	Sym	1:1	2*a*
(7)-(2)	2,3	0	Sn, SS	S	1:1	*d*
(1)-(8)	0	2, 3	SS	U	1:1	*d*
(7)-(8)	2, 3	2, 3	*e*			
(9)-(2)	2, 5	0	Sn, SS	S	1:2[c]	2*a*, 2*c*
(1)-(10)	0	2, 5	SS	U	1:1	2*a*, 2*c*
(9)-(12)	2, 5	2, 5	Sn	Sym	1:1	*d*
(9)-(10)	2, 5	2, 5	St, SSH	Sym	2:1	2*b*, *d*
(5)-(2)	2, 6	0	Sn, SS	S	1:2[c]	*d*
(1)-(6)	0	2, 6	SS	U	1:1	*d*
(5)-(6)	2, 6	2, 6	Sn, SS	Sym	1:1	*d*
(11)-(2)	2, 3, 5	0	Sn, SS	S	1:2[c]	*d*
(1)-(12)	0	2, 3, 5	SS	U	1:1	*d*
(11)-(12)	2, 3, 5	2, 3, 5	Sn, SS	Sym	1:1	*d*
(13)-(2)	2, 3, 5, 6	0	SSH	S	1:1	*d*
(13)-(2)	2, 3, 5, 6	0	St	S	1:2	*d*, *f*
(1)-(14)	0	2, 3, 5, 6	SS	U	2:1	*d*
(13)-(14)	2, 3, 5, 6	2, 3, 5, 6	Sn, St	Sym	1:1	4, 5, 2*b*, *f*

[a] Sn = conventional crystallization from solution; St = crystallization from solution kept saturated with both components and seeded (see Experimental section); SS = solid–solid reaction;[2a] SSH = solid–solid reaction only when heated to 80 °C (see Experimental section). [b] Relative stability in the hydrogen-transfer (redox) equilibrium: S = more stable, U = less stable, Sym = symmetrically substituted. [c] The stoicheiometry is somewhat variable; the ratio lies between 1:1 and 1:2. Such variation suggests that vacancies containing the extra hydroquinone molecule are sometimes incompletely filled and is reminiscent of the behaviour of clathrate-forming compounds such as β-hydroquinone.[13] [d] This paper. [e] Complex too unstable to be isolated. [f] Crystal structure reported in the following paper.

the 2- and 6-position of both the quinone and the hydroquinone rings of the reacting molecules still permits ready complex formation, whereas substitution on the 2- and 5-position of both reactants permits complex formation only under special conditions, and substitution on the 2- and 3-position has thus far prohibited the formation of any complex.

One of the most remarkable results of the studies of polymethylated quinhydrones is that exemplified by the reaction of duroquinone (**13**) with hydroquinone (**2**). A solution in toluene–methanol of equimolar amounts of these two compounds when set aside for several weeks gave only crystals of the unsubstituted complex of (**1**) and (**2**) formed by disproportionation and with no indication of formation of a complex of (**13**) with (**2**). Likewise, when the quinone and hydroquinone were ground together at room temperature or kept in contact, in a capillary tube, there was no evidence of reaction. If the mixture was heated to 80 °C for 2 h, however, conversion into a deep red 1:1 complex was complete, as shown by F.t.i.r. and differential scanning calorimetry. More significant is the observation that nucleation, before grinding of the mixture of the two components, with a few crystals of the product induced complex formation, which then proceeded slowly but completely even at room temperature. Finally, if a saturated solution of (**13**) and (**2**) in ethyl acetate solution in contact with each of the solid components was nucleated with either the 1:2 or the 1:1 complex, there were obtained well formed crystals of the 1:2 complex of (**13**) with (**2**).

The requirement that complex formation be properly nucleated has been observed in the reaction of quinone vapour with single crystals of di- and tetra-methylated hydroquinones described in an earlier paper.[2f] It seems possible that nucleation is required by all such 'solid–solid' reactions of quinones with hydroquinones, but this may not be evident when the reactants are relatively unhindered and have an inherently greater tendency to react. It might be thought that the need for proper nucleation should be greatest when both reagents are relatively non-volatile (*i.e.* have very low vapour pressures). That this is not the controlling factor, however, is shown by a comparison of the rapid reaction between the unmethylated quinone (**1**) and the tetramethylhydroquinone (**14**) with the reluctant companion reaction of the tetramethylquinone (**13**) with unmethylated hydroquinone (**2**) already discussed. In the former case reaction proceeds readily on grinding the components together in the usual manner to give a complex with the quinone and hydroquinone in 2:1 ratio.

Stabilities of Complexes and the Importance of Nucleation in their Decomposition.—All complexes of quinones with hydroquinones in the Table, when kept for a sufficient length of time under ambient conditions, become white, owing to decomposition with loss of the more volatile (quinone) component. The time required for such decomposition varies greatly with structure. Thus decomposition of the unsubstituted complex of (**1**) with (**2**) exposed to the atmosphere at room temperature occurs in about 3 months. At the other extreme an attempt to produce a complex by grinding together the 2,3-substituted quinone (**7**) with the hydroquinone (**8**) gave a red colour attributed to the complex, but the colour faded in a few minutes when the powder was kept in the open atmosphere.

Large crystals of the 1:2 complexes of (**9**) with (**2**) and (**13**)

with (**2**) with well developed faces showed clear evidence, on microscopic examination, of initiation of loss of the quinone from nucleation sites in the various faces.

It might be expected that the stabilities of the quinhydrones with respect to the crystalline components could be correlated with their difficulty of formation. Thus the 2:1 complex of 2,5-dimethylquinone (**9**) with 2,5-dimethylhydroquinone (**10**), formed with difficulty, readily loses the quinone by sublimation at room temperature and reverts to polycrystalline hydroquinone.[2b] We have observed no preferential loss of quinone from any particular crystal face, however. Similar results have been obtained with the other complexes formed only with difficulty: duroquinhydrone (**13**)·(**14**) and the 1:2 complex of duroquinone and hydroquinone [(**13**)·(**2**)]. In contrast, single crystals of the parent (unsubstituted) quinhydrone seem to decompose only after several months when kept open to the atmosphere at room temperature.

Further discussion relating stability of methyl-substituted quinhydrones to crystal structure will be found in the following paper.

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