Structural Influences on the Isomerization of 4-Benzyl- and 4-Allyl-1,2-naphthoquinones to Quinonemethides and their Stereochemistry

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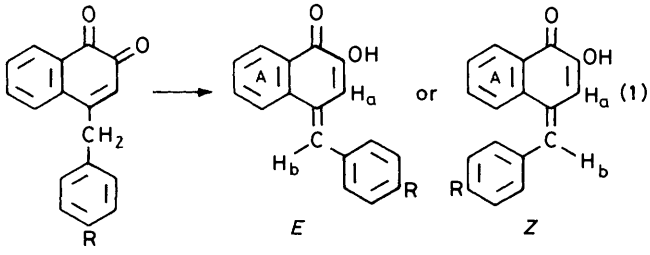
The isomerization of 4-benzyl-1,2-naphthoquinones and 4-allyl-1,2-naphthoquinones to quinonemethides has been studied. The steric interaction and extra π conjugation in the quinonemethide, and acidity of methylene protons of the quinone, are controlling factors for the isomerization. ^{1}H N.m.r. studies suggested that the quinonemethides have the *E* configuration.

It is well known that quinonemethides are some of the most important components or intermediates in the chemistry of lignins,[1] phenolic resins, and wood pigments.[2] Thus a number of quinonemethides have been synthesized by oxidation of phenols or by other elegant methods.[3] Fieser and Fieser reported that 4-benzyl-1,2-naphthoquinone (**1**) isomerized to quinonemethide (**5**) in the presence of sulphuric acid or sodium hydroxide.[4] Recently we found that silica gel was also effective for the isomerization.[5] However, the stereochemistry of compound (**5**) has not been determined. Here we report a controlling factor for the isomerization of 4-benzyl- and 4-allyl-1,2-naphthoquinones to their quinonemethides, and also discuss the stereochemistry of the quinonemethides.

Results and Discussion

Similarly to (**1**), 4-(*p*-chlorobenzyl)- (**2**), 4-(*p*-methoxybenzyl)- (**3**), and 4-(*p*-methylbenzyl)-1,2-naphthoquinone (**4**) could be converted into quinonemethides (**6**)—(**8**), respectively, in high yield by treatment with sulphuric acid [equation (1)].



(**1**) R = H (**5**)
(**2**) R = Cl (**6**)
(**3**) R = OMe (**7**)
(**4**) R = Me (**8**)

The isomerization proceeded even in the presence of 1,2-dimethylimidazole as a base. The time-dependent change of the u.v. spectra of quinones (**1**), (**2**), and (**3**) (9.09×10^{-3}M) in the presence of 1,2-dimethylimidazole (2.10×10^{-3}M) in benzene was measured. All of them showed a distinct isosbestic point at ~500 nm. A typical example is shown in the Figure. From the decrease in the absorbance of the quinones ($\lambda_{max.}$ 530 nm), the relative rates for the isomerization of compounds (**1**), (**2**), and (**3**) were estimated to be 1.00:1.17:0.71, respectively. These results clearly indicate that the acidity of the methylene protons of 4-benzyl-1,2-naphthoquinones influences the ease of this isomerization.

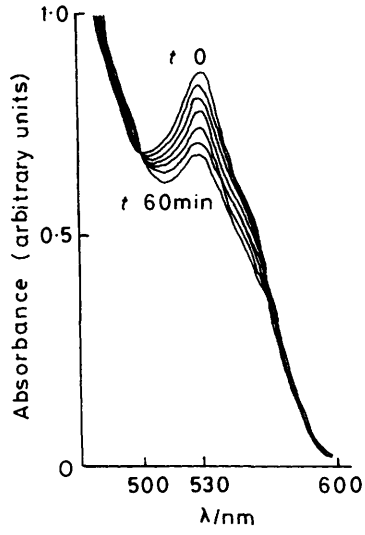


Figure. Visible absorption spectrum of 4-(*p*-methoxybenzyl)-1,2-naphthoquinone (**3**) (9.90×10^{-3}M) in benzene before (0 min) and after (10, 20, 30, 40, 50, and 60 min) the addition of 1,2-dimethylimidazole (2.10×10^{-3}M)

As is shown in equation (1), there are two possible (*E* or *Z*) configuration for the quinonemethides (**5**)—(**8**). In order to determine the stereochemistry, ^{1}H n.m.r. chemical shifts of compounds (**5**)—(**8**) were examined and the results are summarized in Table 1. In the *E* form, the benzylidene proton (H_b) is located in a deshielded region of ring A, while in the *Z* form, H_b is situated far from ring A and should therefore resonate at a higher field than it does for the *E* form. In order to estimate the chemical shift of H_b in the *Z* form, we prepared quinonemethide (**9**) and its deuterium-labelled compound (**9-D**). The $H_{b'}$ on compound (**9**) is in a similar situation to that of H_b in the *Z* form of compounds (**5**)—(**8**).

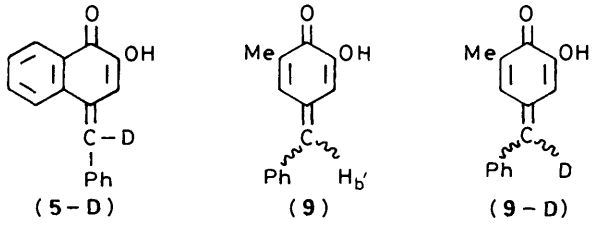


Table 1. ^{1}H N.m.r. chemical shifts of quinonemethides (**5**)—(**8**) in $CDCl_3$ solution (δ-values)[a]

	δ_H					
	H_a	H_b	OH	ArH	Ring protons	Other protons
(**5**)	7.25	7.86	6.86	7.35	7.37—7.65 (2 H, m) 8.04 (1 H, d, *J* 8) 8.20 (1 H, dd, *J* 2 and 8)	
(**6**)	7.25	7.88	6.93	7.42	7.48—7.76 (2 H, m) 8.15 (1 H, d, *J* 8) 8.34 (1 H, dd, *J* 2 and 8)	
(**7**)	7.30	7.82	6.80	6.80 (2 H, d, *J* 9) 7.35 (2 H, d, *J* 9)	7.32—7.60 (2 H, m) 8.02 (1 H, d, *J* 8) 8.20 (1 H, dd, *J* 2 and 8)	3.77 (3 H, s)
(**8**)	7.31	7.87	6.85	7.20 (2 H, d, *J* 8) 7.35 (2 H, d, *J* 8)	7.43—7.68 (2 H, m) 8.07 (1 H, d, *J* 8) 8.25 (1 H, dd, *J* 2 and 8)	2.38 (3 H, s)

[a] *J*-values are in Hz.

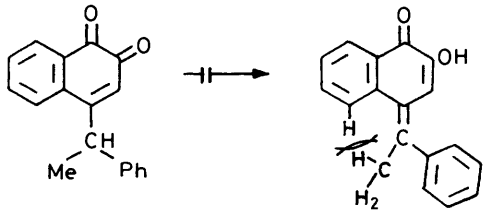
The singlet signal at δ 7.86 observed in compound (**5**) was assigned to H_b by comparison with the ^{1}H n.m.r. spectrum of (**5-D**), while $H_{b'}$ in (**9**) resonated at δ 7.16 [assignment confirmed by comparison with ^{1}H n.m.r. spectrum of labelled derivative (**9-D**)]. The difference in the chemical shifts (Δδ 0.70 p.p.m.) between H_b and $H_{b'}$ suggests that compound (**5**) has the *E* configuration. Other quinonemethides, (**6**)—(**8**), were also *E* isomers, as deduced from the chemical shift of their H_b atom (Table 1).

The theoretical deshielding effect on H_b in (*E*)-(**5**) or (*Z*)-(**5**), according to the ring-current model proposed by Johnson and Bobey,[6] is *ca.* 0.60 p.p.m. for (*E*)-(**5**) and *ca.* 0.25 p.p.m. for (*Z*)-(**5**) [(*E*)-(**5**): ρ 3.65 Å, *z* 0 Å; (*Z*)-(**5**): ρ 4.82 Å, *z* 0 Å; ρ and *z* are two components of the radius vector from the centre of deshielding ring A to H_b, ρ lies in the plane of ring A and *z* is the component along the hexad axis.] The theoretical value for (*E*)-(**5**) is in fairly good agreement with that observed (Δδ 0.70 p.p.m.). From these results it was further confirmed that quinonemethides (**5**)—(**8**) have *E* configuration.

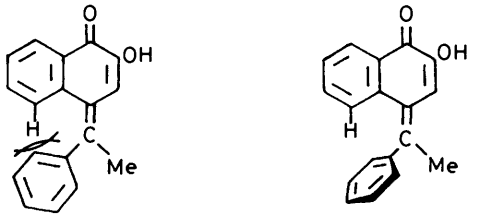
In contrast to quinones (**1**)—(**4**), 4-(α-methylbenzyl)-1,2-naphthoquinone (**10**) and 4-phenethyl-1,2-naphthoquinone (**12**) did not isomerize to quinonemethides and they were recovered unchanged after treatment with sulphuric acid, 1,2-dimethylimidazole, or on a silica gel column [equations (2) and (3)]. As shown in equation (2), there is a steric interaction between *peri*-hydrogen 5-H and the α-methyl group in (*E*)-(**11**), or between 5-H and the phenyl group in (*Z*)-(**11**). In (*Z*)-(**11**), twist of the benzene ring around the Ph–C axis can release this interaction, but the delocalization energy might be minimized by taking a nonplanar structure (*Z*)-(**11′**). Thus both the steric interaction and the effective delocalization of π electrons are important factors for the isomerization of 4-benzyl-1,2-naphthoquinones. The significant feature of the delocalization is also supported by the fact that compound (**12**) did not isomerize; nevertheless there is no such steric repulsion in (*E*)-(**13**) [equation (3)].

We next examined the isomerization of 4-allyl-1,2-naphthoquinones. Treatment of 4-allyl-1,2-naphthoquinone (**14**) with sulphuric acid or aqueous sodium hydroxide afforded a viscous polymeric product. However, when compound (**14**) was passed through a column of silica gel with benzene as eluant, we successfully obtained 4-allylidene-2-hydroxynaphthalen-1(4*H*)-one (**17**) in 41% yield. 4-[(*E*)-But-2-enyl]-(**15**) and 4-(3-methylbut-2-enyl)-1,2-naphthoquinone (**16**) also isomerized on silica gel to give quinonemethides (**18**) (70%) and (**19**) (90%) respectively [equation (4)].

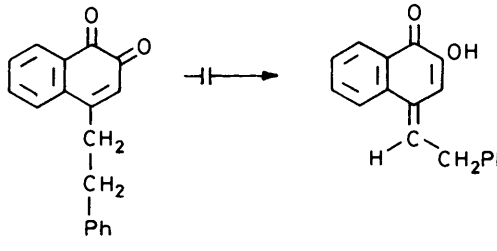
The ^{1}H n.m.r. chemical shifts of compounds (**17**)—(**19**) were also studied. The allylidene protons of product (**17**) were not



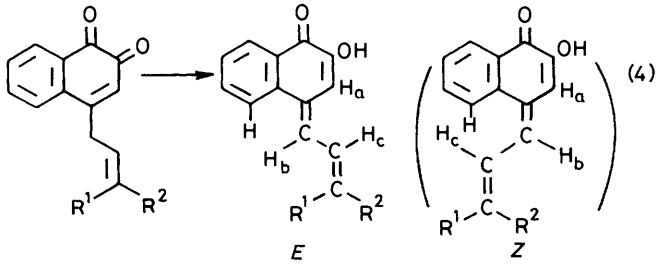
(**10**) (*E*)-(**11**) (2)



(*Z*)-(**11**) (*Z*)-(**11′**)



(**12**) (*E*)-(**13**) (3)



(4)

(**14**) $R^1 = R^2 = H$ (**17**)
(**15**) $R^1 = H, R^2 = Me$ (**18**)
(**16**) $R^1 = R^2 = Me$ (**19**)

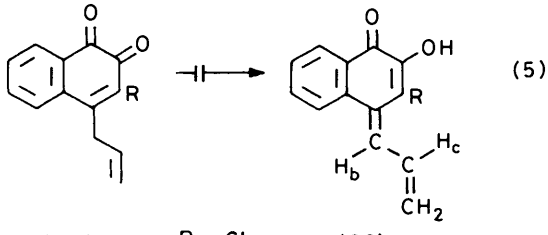
Table 2. ^{1}H N.m.r. chemical shifts of naphthalenones (17)—(19) in $CDCl_3$ solution (δ-values)[a]

	δ_H						
	H_a	H_b	H_c	R^1	R^2	OH	Aromatic
(17)	7.35	*b*	7.00—7.32 (m)	5.81 (1 H, d, *J* 15) 5.66 (1 H, dd, *J* 2 and 9)		6.99	7.43—7.78 (2 H, m) 8.12 1 H, (dd, *J* 2 and 8) 8.35 (1 H, dd, *J*, 2 and 8)
(18)	7.42	7.70 (d, *J* 14)	7.00 (br t, *J* 14)	6.42 (sex, *J* 7 and 14)	2.03 (3 H, d, *J* 7)	7.10	7.48—7.77 (2 H, m) 8.16 (1 H, br d, *J* 8) 8.44 (1 H, (dd, *J* 2 and 8)
(19)	7.40	7.78 (d, *J* 14)	6.69 (d, *J* 14)	2.03 (6 H, s)		6.97	7.52—7.68 (2 H, m) 8.12 (1 H, br d. *J* 8 8.35 (1 H, (dd, *J* 2 and 8)

[a] *J*-values are in Hz. [b] Not determined.

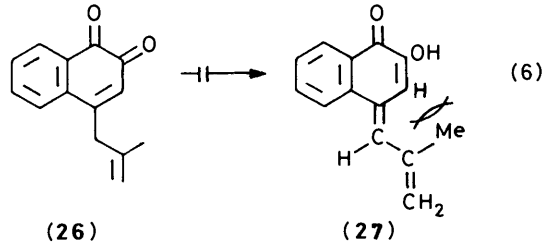
fully assigned due to their complex coupling pattern, but the allylidene protons of compounds (**18**) and (**19**) could be characterized by the spin-decoupling technique and by comparison of their chemical shifts. The chemical shifts are summarized in Table 2. The observed *J* values (14 Hz) between H_b and H_c in both (**18**) and (**19**) indicated that the dihedral angle φ ($H_b\hat{C}C$ and $C\hat{C}H_c$ was nearly 180°.[7] Therefore the vicinal protons (H_b and H_c) are situated in an *s*-trans conformation. This evidence suggested that the C–C bond (H_bC–CH_c) is not free to rotate, and therefore the quinonemethide is planar owing to the conjugation between the quinone ring and the extra double bond in the side-chain.* Examination of molecular models reveals that steric repulsion between *peri*-hydrogen 5-H and H_c is present in the *Z* form, but not in the *E* form. Therefore these quinonemethides also have the *E* configuration.

The postulated restricted rotation around the H_bC–CH_c axis and the proposed *E* structure for compounds (**17**)—(**19**) were supported by the facts that 4-allyl-3-chloro- (**20**), 4-allyl-3-methoxy- (**21**), 4-allyl-3-methyl- (**22**), and 4-(2-methylprop-2-enyl)-1,2-naphthoquinone (**26**) did not isomerize to their corresponding quinonemethides [equations (5) and (6)]. In



(5)

(**20**) R = Cl (**23**)
(**21**) R = OMe (**24**)
(**22**) R = Me (**25**)



(6)

(**26**) (**27**)

these molecules the greater steric repulsion between the substituent group at position 3 and H_c in compounds (**23**)—(**25**) or between the quinonoid proton and the methyl group on the side-chain in compound (**27**) could be operating.

Thus the steric interaction and extra π conjugation in quinonemethides, and the acidity of the methylene protons of the quinone, play an important role in the isomerization.

Experimental

M.p.s were measured on a Yanagimoto micro-melting point apparatus and are uncorrected. ^{1}H N.m.r. spectra were taken with a JEOL MH-100 spectrometer (100 MHz) in $CDCl_3$ solution with tetramethylsilane as internal standard. I.r. spectra were measured with a Hitachi 215 or 250—60 diffraction-grating i.r. spectrophotometer. U.v. spectra were measured with a Hitachi 220A double-beam spectrometer. Column chromatography was performed on silica gel (70—230 mesh, Merck Art. No. 7734).

Materials.—1,2-Naphthoquinone,[8] 3-chloro-,[9] 3-methoxy-,[10] and 3-methyl-1,2-naphthoquinone,[11] were prepared according to the methods described in the literature. The following tin reagents were prepared using previously reported methods: allyltributyltin,[12] (2-methylprop-1-enyl)tributyltin,[12] (*E*)-but-2-enyl(tributyl)tin,[13] and (3-methylbut-2-enyl)tributyltin.[12] 4-Allyl-3-chloro- (**20**), 4-allyl-3-methoxy- (**21**), 4-allyl-3-methyl- (**22**), and 4-(2-methylprop-2-enyl)-1,2-naphthoquinone (**26**) were prepared by the reported method.[14]

Preparation of 4-*Benzyl*-1,2-*naphthoquinone* (**1**).—The reported method for the preparation of the title compound was of mediocre efficiency (overall yield 24%),[15] so we modified the Fieser's method as follows. Aluminium chloride (6.8 g, 0.05 mol) was added in portions to a nitrobenzene (60 ml) solution of 1-naphthol (7.2 g, 0.05 mol) and benzoyl chloride (6.7 g, 0.048 mol) at 0 °C; the mixture was then allowed to warm slowly to 10 °C, and was then stirred for a total of 19 h. After removal of nitrobenzene, 4-benzoylnaphthol was collected (11.0 g, 88%), m.p. 166—168 °C (from benzene–hexane).

A suspension of lithium aluminium hydride (1.0 g, 25 mmol) in dry ether (25 ml) was treated with a solution of aluminium chloride (3.3 g) in dry ether (25 ml).[16] After 5 min, the ethereal solution was treated with a solution of 4-benzoylnaphthol (5 g) and aluminium chloride (2.7 g) in a mixture of dry ether and tetrahydrofuran (50 ml) (1:1 v/v) at such a rate as to produce gentle reflux. After hydrolysis with water (40 ml) and 3M-sulphuric acid (30 ml), 4-benzylnaphthol was isolated as prisms (4.2 g, 90%), m.p. 121—123 °C (lit.,[15] 122.5—123.5 °C).

The naphthol was oxidized by Teuber's method[10] to yield 4-benzyl-1,2-naphthoquinone (**1**) as orange needles (4.1 g, 93%) (overall yield 73%), m.p. 184—185 °C (from benzene–hexane) (lit.,[15] 148 °C); $\nu_{max.}$ (KBr) 1 695w and 1 650 cm^{-1}; $\lambda_{max.}$

* The higher stability of 4-allylidene-2,6-dimethylcyclohexa-2,5-dien-1-one was also explained by the presence of an extra double bond in conjugation (L. K. Dyall and S. Winstein, *J. Am. Chem. Soc.*, 1972, **94**, 2196).

($CHCl_3$) 337, 402, and 518 nm (log ε 3.41, 3.39, and 1.78); δ_H 3.95 (2 H, s), 6.10 (1 H, s), 7.16 (5 H, s), and 7.35—8.00 (4 H, m).

4-(p-*Chlorobenzyl*)-1,2-*naphthoquinone* (**2**).—The title compound was prepared in a similar manner as above except that *p*-chlorobenzoyl chloride was used: *compound* (**2**) formed red needles (overall yield 70%), m.p. 189—190 °C (from benzene–hexane) (Found: C, 71.9; H, 4.0. $C_{17}H_{11}ClO_2$ requires C, 72.22; H, 3.96%); $\nu_{max.}$ (KBr) 1 685w and 1 653vs cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 335, 399, and 519 nm (log ε 4.44, 4.54, and 1.82); δ_H 4.00 (2 H, s), 6.20 (1 H, s), 7.12—7.33 (4 H, m), 7.58—7.64 (3 H, m), and 8.15 (1 H, dd, *J* 8 and 2 Hz).

4-(p-*Methoxybenzyl*)-1,2-*naphthoquinone* (**3**).—The title compound was prepared in a similar manner as above except that *p*-methoxybenzoyl chloride was used: *compound* (**3**) formed orange needles (overall yield 80%), m.p. 160—162 °C (from benzene) (Found: C, 77.5; H, 4.9. $C_{18}H_{14}O_3$ requires C, 77.68; H, 5.07%); $\nu_{max.}$ (KBr) 1 698w and 1 660 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 344, 405, and 516 nm (log ε 4.45, 4.44, and 1.82); δ_H 3.68 (3 H, s), 3.88 (2 H, s), 6.07 (1 H, s), 6.74 (2 H, d, *J* 9 Hz), 7.03 (2 H, d, *J* 9 Hz), 7.45 (3 H, m), and 8.00 (1 H, dd, *J* 8 and 1.5 Hz).

4-(p-*Methylbenzyl*)-1,2-*naphthoquinone* (**4**).—The title compound was prepared in a similar manner as above except that *p*-methylbenzoyl chloride was used: compound (**4**) formed orange-red prisms (overall yield 75%), m.p. 148—150 °C (from benzene); $\nu_{max.}$ (KBr) 1 690 and 1 660vs cm^{-1}; δ_H 2.32 (3 H, s), 3.96 (2 H, s), 6.15 (1 H, s), 7.09 (4 H, s), 7.42—7.56 (3 H, m), and 8.04 (1 H, dd, *J* 8 and 1.5 Hz).

Preparation of 4-(α-*Methylbenzyl*)-1,2-*naphthoquinone* (**10**).—Zinc chloride (6.5 g, 48 mmol) was added to a solution of a mixture of 1-methoxynaphthalene (6.32 g, 40 mmol) and (1-chloroethyl)benzene (6.7 g, 48 mmol) in carbon disulphide (50 ml), and the mixture was then gently refluxed and stirred for 2 h. The reaction mixture was poured into water and extracted with carbon disulphide. The extract was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to give 1-methoxy-4-(α-methylbenzyl)naphthalene (9.1 g, 88%), m.p. 80—82 °C (from methanol). The product was demethylated upon treatment with boron tribromide [17] to afford the corresponding naphthol in 70% yield, which was oxidized with Fremy's salt [10] to yield the *title compound* (**10**) as red prisms (80%), m.p. 126—128 °C (from benzene–hexane) (Found: C, 82.5; H, 5.3. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.38%); $\nu_{max.}$ (KBr) 1 695w and 1 665vs cm^{-1}; δ_H 1.58 (3 H, d, *J* 7 Hz), 4.35 (1 H, q, *J* 7 Hz), 6.50 (1 H, s), 7.18—7.57 (3 H, m), 7.30 (5 H, s), and 8.12 (1 H, dd, *J* 8 and 2 Hz).

Preparation of 4-*Phenethyl*-1,2-*naphthoquinone* (**12**).—Friedel–Crafts reaction of 1-methoxynaphthalene (5.8 g) with phenylacetyl chloride (7.4 g) in the presence of aluminium chloride (6.4 g) was carried out in the manner described above to give 4-phenylacetyl-1-methoxynaphthalene in 95% yield, m.p. 78—79 °C (from methanol). The ketone was reduced with lithium aluminium hydride–aluminium chloride mixture; demethylation with boron tribromide then yielded 4-phenethylnaphthol in 75% yield, m.p. 103—104 °C. The naphthol was oxidized with Fremy's salt [10] to give the *title compound* (**12**) as orange-red prisms in 66% overall yield, m.p. 134—137 °C (from benzene–hexane) (Found: C, 82.2; H, 5.5. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.38%); $\nu_{max.}$ (KBr) 1 695w and 1 660vs cm^{-1}; δ_H 3.01 (4 H, s), 6.37 (1 H, s), 7.31 (5 H, m), 7.57—7.84 (3 H, m), and 8.21 (1 H, d, *J* 8 Hz).

Preparation of 4-*Allyl*-1,2-*naphthoquinone* (**14**).—Allyltributyltin (198 mg, 0.6 mmol) was added to a dichloromethane solution (10 ml) of 1,2-naphthoquinone (79 mg, 0.5 mmol) and BF_3·OEt_2 (213 mg, 1.5 mmol) under nitrogen at −78 °C. The reaction mixture was allowed to warm to 0 °C and was then quenched with saturated aqueous NaCl (10 ml) and extracted with dichloromethane. The extract was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The resulting oil was immediately treated with Fremy's salt to afford the *title compound* (**14**) as orange-yellow needles (80 mg, 81%), m.p. 108—109 °C (from benzene–hexane) (Found: C, 79.0; H, 5.3. $C_{13}H_{10}O_2$ requires C, 78.77; H, 5.09%); $\nu_{max.}$ (KBr) 1 695w and 1 655vs cm^{-1}; δ_H 3.47 (2 H, d, *J* 7 Hz), 5.20—5.36 (2 H, m), 5.82—6.21 (1 H, m), 6.43 (1 H, s), 7.47—7.83 (3 H, m), and 8.18 (1 H, dd, *J* 8 and 2 Hz).

4-[(*E*)-*But*-2-*enyl*]-1,2-*naphthoquinone* (**15**).—(*E*)-But-2-enyl(tributyl)tin (450 mg, 1.2 mmol) was added to a CH_2Cl_2 solution (15 ml) of 1,2-naphthoquinone (158 mg, 1 mmol) and BF_3·OEt_2 (426 mg, 3 mmol) under nitrogen at −78 °C. The mixture was worked up in a similar manner as above to give the *title compound* (**15**) as orange needles (106 mg, 50%), m.p. 124.5—125.5 °C (from benzene–hexane) (Found: C, 79.0; H, 5.9. $C_{14}H_{12}O_2$ requires C, 79.23; H, 5.70%); $\nu_{max.}$ (KBr) 1 698w and 1 658vs cm^{-1}; δ_H 1.65 (3 H, d, *J* 5 Hz), 3.28 (2 H, d, *J* 5 Hz), 5.49 (2 H, m), 6.25 (1 H, s), 7.31—7.26 (3 H, m), and 7.97 (1 H, dd, *J* 8 and 1.5 Hz).

4-(3-*Methylbut*-2-*enyl*)-1,2-*naphthoquinone* (**16**).—(3-Methylbut-2-enyl)tributyltin (143 mg, 0.4 mmol) was added to a CH_2Cl_2 solution (8 ml) of 1,2-naphthoquinone (47.4 mg, 0.3 mmol) and BF_3·OEt_2 (128 mg, 0.9 mmol) under nitrogen at −78 °C. Work-up in a similar manner as above gave the *title compound* (**16**) as orange-red prisms (41 mg, 60%), m.p. 146—148 °C (from benzene–hexane) (Found: C, 79.7; H, 6.1. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%); $\nu_{max.}$ (KBr) 1 695w and 1 660vs cm^{-1}; δ_H 1.73 (3 H, s), 1.78 (3 H, s), 3.38 (2 H, d, *J* 7 Hz), 5.25 (1 H, t, *J* 7 Hz) 6.41 (1 H, s), 7.44—7.78 (3 H, m), and 8.15 (1 H, dd, *J* 8 and 1 Hz).

Isomerization of Quinones with Acid.—A 4-benzyl-1,2-naphthoquinone (**1**)—(**4**) (1.5 mmol) was dissolved in conc. sulphuric acid (4 ml) at 0 °C. After being stirred for a few min at this temperature, the dark red or violet solution was poured into ice. The crystalline yellow product was collected, washed with water, air dried, and recrystallized from benzene or benzene–hexane. Physical properties of the quinonemethide (**5**) were described in our previous paper.[5] ^1H N.m.r. spectral data of quinonemethides are summarized in Table 1. Other physical properties are given in below.

4-(p-*Chlorobenzylidene*)-2-*hydroxynaphthalen*-1(4H)*one* (**6**): yellow needles (70%), m.p. 188—190 °C (Found: C, 72.3; H, 3.9. $C_{17}H_{11}ClO_2$ requires C, 72.22; H, 3.96%); $\nu_{max.}$ 3 340 (OH) and 1 630 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 311 and 396 nm (log ε 4.00 and 4.38).

2-*Hydroxy*-4-(p-*methoxybenzylidene*)*naphthalene*-1(4H)-*one* (**7**): orange-yellow prisms (78%), m.p. 156—159 °C (Found: C, 77.7; H, 5.0. $C_{18}H_{14}O_3$ requires C, 77.68; H, 5.07%); $\nu_{max.}$ (KBr) 3 330 (OH) and 1 625 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 292 and 419 nm (log ε 3.92 and 4.45).

2-*Hydroxy*-4-(p-*methylbenzylidene*)*naphthalen*-1(4H)-*one* (**8**): orange-yellow leaves (80%), m.p. 149—150 °C (Found: C, 82.35; H, 5.5. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.38%); $\nu_{max.}$ (KBr) 3 345 (OH) and 1 630 cm^{-1} (C=O).

The quinones (**10**) and (**12**) were recovered unchanged after treatment with conc. sulphuric acid at 0 °C (95 and 75% recovery, respectively). 4-Allyl-1,2-naphthoquinones (**14**)—(**16**) decomposed upon treatment with conc. sulphuric acid to afford a blackish, viscous, polymeric product.

Isomerization with 1,2-*Dimethylimidazole.*—^1H N.m.r. measurements before and after the addition of an excess of 1,2-

dimethylimidazole to a $CDCl_3$ solution of the quinone (**1**) revealed that compound (**1**) isomerized to the quinonemethide (**5**). No ^1H n.m.r. spectra changes for compounds (**10**) and (**12**) were observed after addition of the imidazole.

Isomerization on a Column of Silica Gel.—4-Allyl-1,2-naphthoquinone (**14**) (50 mg) was chromatographed on a column of silica gel (6.0 g) with benzene as eluant to give 4-*allylidene*-2-*hydroxynaphthalen*-1(4 H)-*one* (**17**) (21 mg) as yellowish-brown prisms, which gradually decomposed at room temperature, m.p. 198—200 °C (decomp.) (Found C, 78.7; H, 5.2. $C_{14}H_{12}O_2$ requires C, 78.77; H, 5.09%); $\nu_{max.}$ (KBr) 3 350 (OH) and 1 625 cm^{-1} (C=O). ^1H N.m.r. data are summarized in Table 2. Other quinones, (**15**) and (**16**), also isomerized, to give quinonemethides (**18**) and (**19**) respectively, by passage through a column of silica gel. Their physical properties are given below and their ^1H n.m.r. data are summarized in Table 2.

4-(*But*-2-*enylidene*)-2-*hydroxynaphthalen*-1(4 H)-*one* (**18**): yellow prisms, m.p. 131—132 °C (from benzene–hexane) (Found: C, 79.2; H, 5.9. $C_{14}H_{12}O_2$ requires C, 79.23; H, 5.70%); $\nu_{max.}$ (KBr) 3 320 (OH) and 1 615 cm^{-1} (C=O); $\lambda_{max.}$ ($CHCl_3$) 310 and 406 nm (log ε 4.12 and 3.53).

2-*Hydroxy*-4-(3-*methylbut*-2-*enylidene*)*naphthalen*-1(4 H)-*one* (**19**): red prisms, m.p. 150—151 °C (from benzene) (Found: C, 79.6; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%); $\nu_{max.}$ 3 340 (OH) and 1 600 cm^{-1} (C=O); $\lambda_{max.}$ 315 and 420 nm (log ε 4.11 and 4.59).

Preparation of Compound (**5-D**).—4-Benzoylnaphthol was reduced with lithium aluminium deuteride–aluminium chloride mixture as described in the preparation of unlabelled compound (**5**). The resulting naphthol was oxidized with Fremy's salt to give 4-(α,α-dideuteriobenzyl)-1,2-naphthoquinone, δ_H 6.25 (1 H, s), 7.26—7.37 (5 H, m), 7.50—7.67 (3 H, m), and 8.20 (1 H, br d, *J* 8 Hz). Treatment of the quinone with conc. sulphuric acid at 0 °C gave the quinomethide (**5-D**) as yellow needles, δ_H 6.93 (1 H, s, OH), 7.30 (1 H, s), 7.38 (5 H, s), 7.40—7.67 (2 H, m), 8.07 (1 H, d, *J* 8 Hz), and 8.25 (1 H, dd, *J* 8 and 2 Hz).

Preparation of 4-*Benzylidene*-2-*hydroxy*-6-*methylcyclohexa*-2,5-*dien*-1-*one* (**9**) *and its Deuterium Derivative* (**9-D**).—Reduction of 5-benzoyl-3-methylpyrocatechol[18] with lithium aluminium hydride–aluminium chloride mixture gave 5-benzyl-3-methylpyrocatechol in 93% yield. This compound was oxidized with silver(I) oxide to afford 5-benzyl-3-methyl-1,2-benzoquinone as reddish-brown needles, m.p. 78 °C; $\nu_{max.}$ (KBr) 1 675s, 1 595vs, 1 580m, 1 380s, and 695s cm^{-1}; δ_H (CCl_4) 1.90 (3 H, s), 3.69 (2 H, s), 6.04 (1 H, br s), 6.55 (1 H, m), and 7.12—7.45 (5 H, m).

The quinone (34 mg) was chromatographed on silica gel (benzene as eluant) to give the *title acyloin* (**9**) as yellow leaves (33 mg), m.p. 128—130 °C (Found: C, 79.1; H, 5.9. $C_{14}H_{12}O_2$ requires C, 79.23; H, 5.70%); $\nu_{max.}$ 3 325 (OH), 1 605 (C=O), 1 545, and 1 350 cm^{-1}; δ_H 2.09 (3 H, s), 6.87 (1 H, s, OH), 7.06 (2 H, s), 7.16 (1 H, s), and 7.40 (5 H, m). Deuterium derivative (**9-D**) was prepared by the same procedures as for compound (**9**) except that a lithium aluminium deuteride–aluminium chloride mixture was used as the reducing agent. The ^1H n.m.r. data of compound (**9-D**) are δ_H 2.10 (3 H, s), 6.92 (1 H, s, OH), 7.06 (2 H, s), and 7.42 (5 H, m).

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