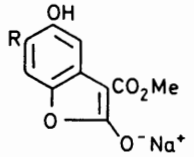
The Reaction of Hydroquinone and Monosubstituted Hydroquinones with Dimethyl Chloromalonate

By **Andrew H. Renfrew,* Stephen B. Bostock,** and (in part) **Christopher M. Ecob,** Imperial Chemical Industries Ltd., Organics Division, Hexagon House, Blackley, Manchester M9 3DA

Hydroquinone and monosubstituted hydroquinones free from $-I,-M$ groups react with dimethyl chloromalonate in methanolic sodium methoxide solution to give 2-oxido-benzo[*b*]furan derivatives (1). The mechanism of this base catalysed *C*-alkylation is interpreted in terms of initial mono-*O*-alkylation followed by fragmentation and 1,4-addition of dimethyl sodiomalonate to the nascent 1,4-benzoquinone so formed. The procedure furnishes, in moderate to high yield, products which cannot be prepared readily by direct nucleophilic addition to 1,4-benzoquinones.

HYDROQUINONE is known to react with dimethyl chloromalonate in methanol, with sodium methoxide as base, to give sodium 5-hydroxy-3-methoxycarbonylbenzo[*b*]-furan-2-olate (1; R = H), thereby providing a novel route to homogentisic acid (2).[1]



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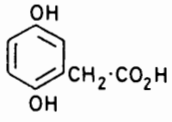


(2)

This apparent *C*-alkylation of the ambident anion of hydroquinone is at variance with the other numerous base-catalysed alkylations reported,[2] where only *O*-alkylation has been observed. Accordingly the scope, synthetic utility, and pathway of this anomalous reaction have been studied.

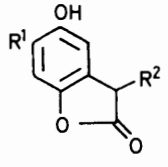
A number of monosubstituted hydroquinones and other aromatic phenolic compounds were treated with dimethyl or diethyl chloromalonate in alcoholic media with sodium alkoxide as base. Of the hydroquinones examined, methoxy, methyl, butyl, and chloro derivatives gave *C*-alkylated products, whereas carboxy and carboxymethyl derivatives yielded only *O*-alkylated products. Of the other aromatic phenols studied, *p*-methoxyphenol, α-naphthol, β-naphthol, resorcinol, and catechol gave only *O*-alkylated products, as did phenol itself.[3]

The reactions which resulted in *C*-alkylation were generally characterised by a pronounced colour change, mild exothermicity, and (other than that of t-butylhydroquinone) a heavy precipitate at the end of the reaction, after partial removal of the solvent (see Experimental section). In all these reactions the hydroquinone species was treated with 0.5 equiv. of chloro-compound to facilitate monoalkylation. In most of the other cases where *O*-alkylation was found, the experiments were re-run with equimolar amounts of reactants to aid the work-up.

The 2-oxido-benzo[*b*]furan salts were grey solids with m.p. >300°, and, unlike the *O*-alkylated products described above, were generally poorly soluble in methanol. The strong electron donation of the 2-oxido-group in compounds of type (1) resulted in characteristic ester bands at *ca.* 1 690 cm^{-1} in the i.r., which assisted identification. T.l.c. also proved useful, as benzo[*b*]furan salts (1) moved only slightly off the base line (see Experimental section). Structural elucidation was completed by ^1H n.m.r. spectroscopy, and, owing to crystallisation difficulties, by transformation[1] into the more easily handled benzofuran-2(3*H*)-ones (3; R^2 = H or CO_2Me).

The *O*-alkylated products (which had higher R_F values than the starting phenols) showed one, or more usually two, carbonyl bands above 1 730 cm^{-1}. Doublet carbonyl absorption has been noted for malonates and ascribed to vibrational coupling.[4] Where *O*-alkylation was found the crude product was examined by i.r. spectroscopy and by t.l.c. but in no case was any *C*-alkylated product detected. The mixture from carboxymethylhydroquinone was not amenable to study by i.r. spectroscopy owing to strong absorption by the starting material in the 1 690 cm^{-1} region. However assessments by the general criteria discussed above were in keeping with *O*-alkylation for this reaction.

Of the compounds studied only hydroquinone and certain of its derivatives gave *C*-alkylation. Monosubstituted derivatives could furnish one of three



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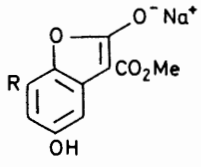

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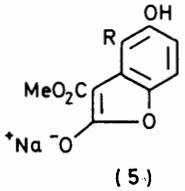

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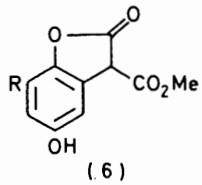


(6)

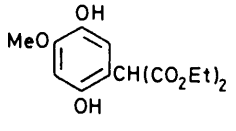
possible isomers [(1), (4), and (5)] or a mixture. Methoxyhydroquinone gave, in 87% yield, isomer (1; R = OMe) only, as judged by the n.m.r. spectrum of both the salt and the protonated derivative (3; R^1 = OMe, R^2 = CO_2Me). T.l.c. of the latter species confirmed this.

Chlorohydroquinone behaved similarly: the salt (1; R = Cl) was the only isomer found, but with a yield of isolated product of only 54%, other isomers cannot be ruled out.

Methylhydroquinone, on the other hand, gave isomers (1; R = Me) and (4; R = Me) in the ratio *ca.* 3 : 4. The n.m.r. spectrum of this mixture showed two different methyl resonances, two aromatic singlets, indicative of the 2,5-orientation (1; R = Me) and two doublets, *J* 2 Hz, indicative of the 2,6-orientation (4; R = Me).[5]

The product from t-butylhydroquinone was isolated in only 32% yield, possibly owing to the solubilising effect of the t-butyl group. The n.m.r. spectrum showed one t-butyl signal at δ 1.32 and one methyl ester resonance at δ 3.64. The aromatic protons displayed a clean pair of doublets, *J* 2 Hz, at δ 6.12 and 6.68, respectively, in keeping with isomer (4; R = Bu^t). N.m.r., t.l.c., and g.l.c. of the protonated derivative (6; R = Bu^t) showed no evidence of more than one isomer. The i.r. spectrum of the βγ-unsaturated lactone (6; R = Bu^t), however, did show two bands in the 1 800 cm^{-1} region, but this is known to occur with lactones.[6]

The product distribution of the unsymmetrical hydroquinones was not inconsistent with a nucleophilic addition mechanism to a 1,4-benzoquinone derivative.[7] Quinones bearing strongly electron-donating substituents are known to give primarily the 2,5-isomer,[8,9] *e.g.* methoxybenzoquinone and diethyl malonate [10] are reported to give only the 2,5-disubstituted isomer (7), albeit in low yield. Moreover the 1,4-addition of thiols to methylbenzoquinone is known to furnish the 2,5- and 2,6-isomers. Gates *et al.*[8] found the 2,5-isomer to be the major product, but with a low total recovery, while Georgian and Skaletzky,[11] using a different thiol, found the reverse situation.



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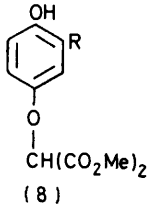
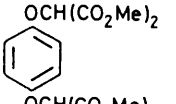


(8)

Support for a quinone addition mechanism was found in a more detailed examination of the original reaction between hydroquinone and dimethyl chloromalonate. A relatively high yield (84.8%) of isolated benzo[*b*]furan (1; R = H) was obtained, while a suspiciously low yield (5.3%) of the mono-*O*-alkylated product (8; R = H), as determined by g.l.c., was found.

The only other products present to any extent were the bis-*O*-alkylated species (9) (1.9%) and tetramethyl ethylenetetracarboxylate (10) (3.2%) as determined by g.l.c. Compounds of type (10) are known self-condensation products of dialkyl halogenomalonates.[3] in basic media.

That *C*-alkylation can proceed *via* *O*-alkylation was confirmed by synthesising dimethyl *p*-hydroxyphenoxymalonate (8; R = H) and adding sodium methoxide to this compound in methanol. The colourless solution immediately turned dark green and yielded the salt (1; R = H), which was characterised by chromatographic and spectroscopic techniques. A possible mechanism is shown in the Scheme.



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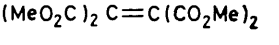
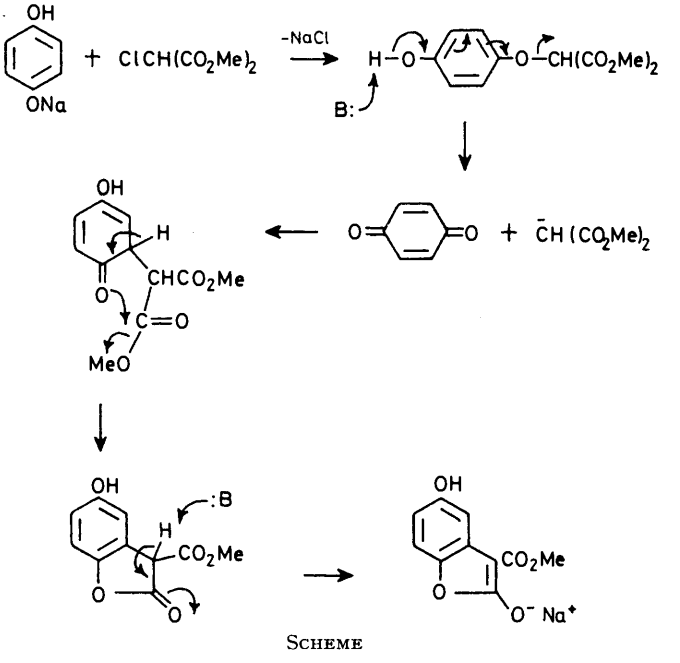


(10)

The mechanism is critically dependent on the nature of both species since, under basic conditions, hydroquinone undergoes *O*-alkylation with a range of alkylating agents [2] and dimethyl chloromalonate is known to react with phenols at oxygen.[12] The role of both the



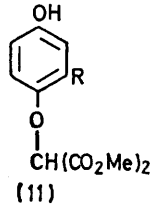
SCHEME

para-hydroxy and malonate functional groups is therefore explained. The former provides the mechanistic trigger and the latter a resonance-stabilised anion. As the stability of a carbanion is directly related to the strength of its conjugate acid,[13] consideration of the relative acid strengths of diethyl malonate (pK_a *ca.* 13) and ethyl acetate (pK_a *ca.* 24.5) [14] reveals why only the malonates are cleaved.[2]

Benzo[*b*]furan salts (1), therefore, are formed *via* initial mono-*O*-alkylation followed by fragmentation and 1,4-addition of dimethyl sodiomalonate to the nascent 1,4-benzoquinone so formed. The final steps are intramolecular cyclisation and enolisation.

Monosubstituted hydroquinones could form two isomeric phenoxymalonates (8) and (11). In the cases of carboxy- and carboxymethyl-hydroquinones, where only *O*-alkylation was observed, compounds (8; R = CO_2H) and (8; R = CO_2Me) were isolated, respectively. Both

products were subsequently shown not to give oxidobenzo[*b*]furan salts of type (1) under the reaction conditions. Hence it appears that a $-I,-M$ group *ortho* to the hydroxy-group of dimethyl *p*-hydroxyphenoxymalonates (8) inhibits this transformation. In contrast the high yields of *C*-alkylated products from methoxy- and methyl-hydroquinone suggest that in these cases the respective intermediates (8) and (11) are fragmented. Chloro- and t-butyl-hydroquinone, on the other hand, gave only moderate yields of *C*-alkylated products. Although no new volatile species was found on g.l.c. analysis of the reaction filtrates, the possibility exists that one or more of the compounds (8; R = Cl or Bu^t) or compounds (11; R = Cl or Bu^t) does not cleave smoothly.



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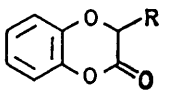

(12)

Methylhydroquinone gave an isomer distribution in line with electronic predictions and previous results.[8,9] t-Butylhydroquinone behaved differently giving only isomer (4; R = Bu^t), and this can be explained by the steric influence of the bulky alkyl group on the adjacent carbonyl group. Previous authors [8] have claimed that only the 3-position (not the 5- and 6-positions) is sensitive to steric factors when monosubstituted benzoquinones are subjected to nucleophilic addition.

The proposed mechanism precludes base-catalysed *C*-alkylation of resorcinol. G.l.c.–mass spectrometry was used to analyse the three major products from the reaction of resorcinol and diethyl chloromalonate; the spectra were consistent with *O*-alkylation (see Experimental section). Other spectral techniques failed to reveal a *C*-alkylated product.

In principle, catechol can undergo *C*-alkylation, although conjugate 1,4-addition [15] to 1,2-benzoquinone cannot lead to a benzo[*b*]furan derivative. The crude reaction mixture in this case was acidified with mineral acid and examined by i.r. spectroscopy, but failed to show a band in the 1 800 cm^{-1} region, ruling out a γ-lactone system and therefore 1,6-addition to 1,2-benzoquinone. The two major products of the reaction were, on the basis of g.l.c.–mass spectrometry, identified as methyl 1,4-benzodioxin-2(3*H*)-one (12; R = CO_2Me) and its demethoxycarbonylated derivative (12; R = H). Intramolecular cyclisation apparently dominates fragmentation in this case.

Nucleophilic additions of dialkyl sodiomalonates to 1,4-benzoquinone and its monosubstituted derivatives are generally unproductive, with diethyl malonate and 1,4-benzoquinone themselves giving only tars.[16] The nascent generation of both the quinone and the malonate anion, within each other's sphere of influence is believed to be responsible for success in this case. Hence this reaction enables hydroquinone and, on the basis of results so far, monosubstituted derivatives, free from $-I,-M$ groups to furnish, in moderate to high yield, *C*-alkylated products which cannot be prepared readily by direct nucleophilic addition to 1,4-benzoquinones.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 177 spectrophotometer (Nujol mulls). ^1H N.m.r. spectra were taken with a Varian HA-100 or a Perkin-Elmer R32 90 MHz spectrophotometer. Mass spectra were taken with an A.E.I. MS9 and with a Pye 104–A.E.I. MS30 gas chromatograph–mass spectrometer [S.E. 301 (10%) 18-in glass column, temp. 50—280° (16° min^{-1})]. Analytical g.l.c. was carried out with a Pye–Unicam G.C.D. chromatograph equipped as described above, unless otherwise stated, and t.l.c. was performed on Eastman Chromagram Sheet using monochlorobenzene–acetone (80 : 20) as eluant. Sodium chloride was determined by potentiometric titration with standard silver nitrate solution. Methanol refers to commercial analytical reagent grade (water content $<0.05\%$). All yields are based on the initial amount of alkylating agent.

General Alkylation Procedure.—The phenol (0.2 mol) was added, under nitrogen, to a solution of sodium methoxide (0.2 mol) in methanol (230 ml). Dimethyl chloromalonate (Fluka) (0.2 mol) was added, all at once, and the mixture stirred at room temperature for 2 h, heated under reflux for a further 2 h, and finally rendered acidic with glacial acetic acid.

Dimethyl p-*Methoxyphenoxymalonate.*—This was obtained from *p*-methoxyphenol and isolated by distilling to dryness to give a crude oil which was fractionally distilled to give the *product* (35%) as a yellow oil (b.p. 140° at 0.2 mmHg); $\nu_{max.}$ 1 772 and 1 740 cm^{-1} (ester C=O); $\delta(CDCl_3)$ 3.69 (3 H, s, OMe), 3.78 (6 H, s, CO_2Me), 5.12 (1 H, s, O–CH<), and 6.70—6.98 (4 H, dd, *J* 8 Hz, ArH) (Found: C, 56.3; H, 5.7%; M^+, 254. $C_{12}H_{14}O_6$ requires C, 56.7; H, 5.6%; *M*, 254).

Dimethyl β-*Naphthyloxymalonate.*—This was obtained from β-naphthol and isolated by crystallisation from the reaction medium, after removing part of the solvent; the *product* (68%) crystallised from methanol as white needles, m.p. 106°; $\nu_{max.}$ 1 772 and 1 746 cm^{-1} (ester C=O); $\delta(CDCl_3)$ 3.73 (6 H, s, CO_2Me), 5.33 (1 H, s, OCH<), 7.10 (1 H, d, *J* 2 Hz, ArH-1), and 7.18—7.78 (6 H, m, other ArH) (Found: C, 66.1; H, 5.2. $C_{15}H_{14}O_5$ requires C, 65.7; H, 5.2%).

Dimethyl α-*Naphthyloxymalonate.*—This was obtained from α-naphthol with isolation as for the β-isomer; the *product* (50%) crystallised from methanol as white needles, m.p. 90°; $\nu_{max.}$ 1 770 and 1 740 cm^{-1} (ester C=O); $\delta(CDCl_3)$ 3.78 (6 H, s, CO_2Me), 5.32 (1 H, s, OCH<), 6.69 (1 H, d, *J* 8 Hz, ArH-2), 7.10—7.83 (5 H, m, ArH), and 8.28—8.48 (1 H, m, ArH-8) (Found: C, 66.0; H, 5.3. $C_{15}H_{14}O_5$ requires C, 65.7; H, 5.2%).

Reaction of Resorcinol with Diethyl Chloromalonate (Aldrich).—This was performed by the general procedure, in ethanol as solvent, and the product isolated by distilling to low bulk, quenching in water and extracting into toluene. The organic layer was washed, dried, and distilled to give an oil (58%) which was shown by t.l.c. and g.l.c. to comprise three major products. As attempted fractional distillation was not successful the mixture was examined by g.l.c.–mass spectrometry [S.E. 301 (10%) 5-ft glass column, temp. 50—300° (16° min^{-1})]. The products were

tentatively identified as diethyl *m*-hydroxyphenoxymalonate (*m/e* 268, 195, 149, and 123); diethyl *m*-(ethoxycarbonylmethoxy)phenoxymalonate (*m/e* 354, 310, 281, and 255); and 1,3-*bis*(*diethoxycarbonylmethoxy*)*benzene* (*m/e* 426, 353, 307, and 281).

Reaction of Catechol with Dimethyl Chloromalonate.—To a solution of sodium methoxide (0.2 mol) in methanol (230 ml) was added, with stirring, under nitrogen, catechol (22 g, 0.2 mol) and the solution was cooled to 25°. Dimethyl chloromalonate (17.4 g of 96%; 0.1 mol) was added, all at once (no colour change or exothermicity observed), and the mixture was stirred for 1 h at 25° and then heated under reflux for 4 h. Glacial acetic acid (10 ml) was added, the solvent (175 ml) removed by distillation, the inorganic salts removed by filtration, and the filtrates taken to dryness to give a crude oil. The oil was taken into ether, and washed in turn with dilute hydrochloric acid and with water. Separation and drying (Na_2SO_4) gave the product (15.2 g). T.l.c. and g.l.c. showed the mixture to comprise two major new products which on the basis of g.l.c.–mass spectrometry were identified as 1,4-benzodioxin-2(3*H*)-one (*m/e* 150, 122, and 121) and 3-carboxymethyl-1,4-benzodioxin-2(3*H*)-one (*m/e* 208, 176, 149, and 121). The structure of the former product was confirmed by g.l.c. comparison with an authentic sample.[17]

1,4-*Bis*(*dimethoxycarbonylmethoxy*)*benzene.*—To sodium methoxide (0.1 mol) in methanol (230 ml), at 40°, were added, under nitrogen, hydroquinone (5.5 g, 0.05 mol) and dimethyl chloromalonate (17.4 g of 96%; 0.1 mol) and the mixture was heated under reflux for 1.5 h. Methanol (110 ml) was removed by distillation, and the residue quenched in ice–water (400 ml) containing concentrated hydrochloric acid (5 ml) to give a slightly sticky white precipitate. The solid was isolated by filtration, washed with methanol and with water and dried to give the *product* (5.1 g, 28%). Crystallisation from toluene gave white needles, m.p. 161°; $\nu_{max.}$ 1 760 and 1 748 cm^{-1} (ester C=O); $\delta[(CD_3)_2SO]$ 3.71 (12 H, s, CO_2Me), 5.62 (2 H, s, $OCH<$), and 6.89 (4 H, s, ArH) (Found: C, 51.7; H, 5.1%; M^+, 370. $C_{16}H_{18}O_{10}$ requires C, 51.9; H, 4.9%; *M*, 370).

Dimethyl p-*Hydroxyphenoxymalonate.*—Hydroquinone (11 g, 0.1 mol), potassium hydroxide (5.6 g, 0.1 mol), toluene (250 ml), and water (4 ml) was stirred and heated under reflux for 1.5 h. Solvent (40 ml) was removed by distillation, dimethyl chloromalonate (17.4 g of 96%; 0.1 mol) was added and the suspension was heated under reflux for a further 6 h. After cooling the mixture was filtered and the filtrate distilled to remove solvent and unchanged chloro-compound to give an oil. The oil was dissolved in methanol (20 ml) and allowed to crystallise fractionally during 2.5 months. The third fraction collected was the desired *product* (60 mg), m.p. 86°; $\nu_{max.}$ 3 490 (OH), 1 770, and 1 735 cm^{-1} (ester C=O); $\delta[(CD)_3SO]$ 3.70 (6 H, s, CO_2Me), 5.45 (1 H, s, $OCH<$), 6.56—6.91 (5 H, dd, *J* 8 Hz, ArH), and 9.10br (1 H, s, OH) (Found: C, 55.4; H, 5.2%; M^+, 240. $C_{11}H_{12}O_6$ requires C, 55.0; H, 5.0%; *M*, 240).

Methyl Ethylenetetracarboxylate.—This was prepared according to the published method; m.p. 121° (lit.,[18] 121°).

Reaction of Chlorohydroquinone with Dimethyl Chloromalonate.—Sodium (2.3 g, 0.1 mol) was dissolved in methanol (120 ml) and the solution cooled to 30°. Chlorohydroquinone (14.5 g, 0.1 mol) was added, under nitrogen, and the suspension stirred for 15 min to give a dark orange solution. Finally, at 25°, was added, all at once, dimethyl chloromalonate (8.7 g of 96%; 0.05 mol). A dark green colour was produced followed by a rise in temperature to 31°. The mixture was stirred for 2 h, heated under reflux for a further 4 h, then methanol (90 ml) was removed by distillation, glacial acetic acid (3 ml) added, and the product chilled in ice. The solid was collected by filtration, washed with methanol and with ether, and dried to give *sodium* 6-*chloro*-5-*hydroxy*-3-*methoxycarbonylbenzo*[b]*furan*-2-*olate* (1; R = Cl) (10 g) contaminated with sodium chloride. The solid was ground and shown by analysis to contain sodium chloride (2.9 g), giving product (7.1 g, 54%), m.p. >300°; $\nu_{max.}$ 3 440 (OH) and 1 692 cm^{-1} (ester C=O); $\delta[(CD_3)_2SO]$ 3.62 (3 H, s, CO_2Me), 6.76 (1 H, s, ArH-7), and 6.95 (1 H, s, ArH-4).

Treatment with phosphoric acid as previously described [1] gave 6-*chloro*-5-*hydroxybenzofuran*-2(3H)-*one* (3; R^1 = Cl, R^2 = H), which crystallised from toluene as off-white needles, m.p. 164°; $\nu_{max.}$ 3 422 (OH) and 1 795 cm^{-1} (lactone C=O); $\delta[(CD_3)_2SO]$ 3.85 (2 H, s, CH_2), 6.97 (1 H, s, ArH-4), 7.21 (1 H, s, ArH-7), and 9.95br (1 H, s, OH) (Found: C, 52.1; H, 2.7; Cl, 19.0%; M^+, 184. $C_8H_5ClO_3$ requires C, 52.1; H, 2.7; Cl, 19.2%; *M*, 184).

Reaction of Methylhydroquinone with Dimethyl Chloromalonate.—Sodium (2.3 g, 0.1 mol) was dissolved in methanol (230 ml) and the solution cooled to 30°. Methylhydroquinone (12.4 g, 0.1 mol) was added, under nitrogen, and the suspension stirred for 5 min to give a pale orange solution. Finally at 25° was added, all at once, dimethyl chloromalonate (8.7 g of 96%; 0.05 mol) (temperature rise of 8° noted). The mixture was stirred for 1 h, then heated under reflux for 4 h. Methanol (160 ml) was distilled off, glacial acetic acid (6 ml) added, and the mass set aside for 18 h. The solid was filtered off, washed with a little methanol, and dried to give a mixture of sodium 5-hydroxy-2-methoxycarbonyl-6- and -7-methylbenzo[*b*]furan-2-olates (10.6 g) (4; R = Me) and (1; R = Me) in the ratio 4 : 3. The solid was ground and shown by analysis to contain sodium chloride (2.6 g), giving product (8.0 g, 66%), m.p. >300°; $\nu_{max.}$ 3 540, 3 480 (OH), and 1 694 cm^{-1} (ester C=O); $\delta[(CD_3)_2SO]$ 2.04 and 2.10 (3 H, two s, ArMe), 3.62 (3 H, s, CO_2Me), 5.96 and 6.60 (two d, *J* 2 Hz, ArH), 6.51 and 6.81 (two s, ArH), and 8.30 (1 H, s, OH).

Treatment with dilute hydrochloric acid, as previously described,[1] gave a mixture of 5-hydroxy-3-methoxycarbonyl-6- and -7-methylbenzofuran-2(3*H*)-ones (3; R^1 = Me, R^2 = CO_2Me) and (6; R = Me) which crystallised from toluene as white needles, m.p. 136—143°; $\nu_{max.}$ 3 400 (OH), 1 795 (lactone C=O), and 1 740 cm^{-1} (ester C=O); $\delta(CDCl_3)$ 2.22 (3 H, s, ArMe), 3.65 and 3.82 (3 H, s, CO_2Me), 3.80br (1 H, s, OH), 4.59 (1 H, s, CH–CO), and 6.51—6.70 (2 H, m, ArH) (Found: C, 59.3; H, 4.3%; M^+, 222. Calc. for $C_{11}H_{10}O_5$: C, 59.5; H, 4.5%; *M*, 222).

Reaction of Methoxyhydroquinone with Dimethyl Chloromalonate.—Sodium (1.15 g, 0.05 mol) was dissolved in methanol (115 ml) and the solution cooled to 30°. Methoxyhydroquinone (7.0 g, 0.05 mol) was added, under nitrogen, and then the solution was stirred for 15 min. Finally at 25° was added, all at once, dimethyl chloromalonate (4.4 g, 0.025 mol). A colour change from brown to deep blue was observed followed by a rise in temperature to 33°, and after stirring for 1 h, a precipitate had formed. The mixture was then heated under reflux for 4 h, methanol (90 ml) was distilled off, glacial acetic acid (6 ml) was added, and the suspension was cooled to 0° in an ice-bath. The solid was collected by filtration, washed with methanol, and dried to give sodium 5-hydroxy-6-methoxy-3-methoxy-

carbonylbenzo[*b*]furan-2-olate (1; R = OMe) (6.7 g). The solid was ground and shown by analysis to contain sodium chloride (0.7 g), giving product (6.0 g, 87%), m.p. >300°; $\nu_{max.}$ 3 260 (OH) and 1 692 cm^{-1} (ester C=O); δ[$(CD_3)_2SO$] 3.59 (3 H, s, OMe), 3.66 (3 H, s, CO_2Me), 6.55 (1 H, s, ArH-7), and 6.83 (1 H, s, ArH-4).

Treatment with dilute hydrochloric acid, as previously described,[1] gave *5-hydroxy-6-methoxy-3-methoxycarbonylbenzofuran-2(3H)-one* (3; R^1 = OMe, R^2 = CO_2Me) which crystallised from methanol as white needles, m.p. 146°; $\nu_{max.}$ 3 490 (OH), 1 805 (lactone C=O), and 1 728 cm^{-1} (ester C=O); δ($CDCl_3$) 3.82 (3 H, s, OMe), 3.92 (3 H, s, CO_2Me), 4.61 (1 H, s, OCH<), and 6.72 and 6.96 (2 H, s, ArH) (Found: C, 55.3; H, 4.0%; M^+, 238. $C_{11}H_{10}O_6$ requires C, 55.5; H, 4.2%; *M*, 238).

Reaction of Carboxyhydroquinone with Dimethyl Chloromalonate.—Sodium (4.6 g, 0.2 mol) was dissolved in methanol (230 ml) and the solution cooled to 35°. Carboxyhydroquinone (15.4 g, 0.1 mol) was added, under nitrogen, with stirring, and at 25°, dimethyl chloromalonate (17.4 g of 96%; 0.1 mol) was then added. The mixture was stirred for 1 h, then heated under reflux for 3 h. Methanol (155 ml) was removed by distillation, and the suspension cooled to 20° and filtered to remove sodium chloride (4.2 g). The filtrates were quenched in ice–water (400 ml) containing 2N-hydrochloric acid (50 ml). The precipitate was collected, washed with water, and dried to give *dimethyl 3-carboxy-4-hydroxyphenoxymalonate* (8; R = CO_2H) (17 g, 60%). Recrystallisation from toluene gave off-white needles, m.p. 130°; $\nu_{max.}$ 2 600 (dimeric OH) 1 780, 1 752 (ester C=O), and 1 675 cm^{-1} (H-bonded acid C=O); δ($CDCl_3$) 3.86 (6 H, s, CO_2Me), 5.21 (1 H, s, OCH<), 6.95 (1 H, d, *J* 9 Hz, ArH-5), 7.18—7.38 (1 H, dd, *J* 9 and 2 Hz, ArH-6), 7.50 (1 H, d, *J* 2 Hz, ArH-2), and 10.45 (2 H, s, labile hydrogens) (Found: C, 50.9; H, 4.3%; M^+, 284. $C_{12}H_{12}O_8$ requires C, 50.7; H, 4.3%; *M*, 284).

Reaction of Carboxymethylhydroquinones with Dimethyl Chloromalonate.—Sodium (1.15 g, 0.05 mol) was dissolved in methanol (230 ml) and the solution cooled to 30°. Carboxymethylhydroquinone (8.4 g, 0.05 mol) was added, under nitrogen, with stirring, and at 25° dimethyl chloromalonate (8.7 g of 96%; 0.05 mol) was then added. No temperature rise or pronounced colour change was noted. The mixture was stirred for 1 h, then heated under reflux for 3 h. After cooling glacial acetic acid (6 ml) was added, and the solvent removed to give a greenish-yellow gum, which solidified on trituration with aqueous methanol. The solid was isolated in the usual way, washed with aqueous methanol, and dried to give *dimethyl 4-hydroxy-3-methoxycarbonylphenoxymalonate* (8; R = CO_2Me) (6.2 g, 42%). Recrystallisation from methanol gave white needles, m.p. 62°; $\nu_{max.}$ 3 120 (H-bonded OH), 1 790, 1 780, and 1 760 (ester C=O) and 1 688 cm^{-1} (H-bonded ester C=O); δ($CDCl_3$) 3.80 (6 H, s, CO_2Me), 3.90 (3 H, s, CO_2Me), 5.16 (1 H, s, OCH<), 6.90 (1 H, d, *J* 9 Hz, ArH-5), 7.10—7.31 (1 H, dd, *J* 9 and 2 Hz, ArH-6), 7.41 (1 H, d, *J* 2 Hz, ArH-2), and 10.43 (1 H, s, OH).

Reaction of t-Butylhydroquinone with Dimethyl Chloromalonate.—Sodium (2.3 g, 0.1 mol) was dissolved in methanol (230 ml) and the solution cooled to 30°. t-Butylhydroquinone (16.6 g, 0.1 mol) was added, under nitrogen, with stirring, and, at 25°, dimethyl chloromalonate (8.7 g, 0.05 mol) was then added. The colour changed from yellow to dark brown and a temperature rise of 8° was noted. The mixture was stirred for 2 h, then heated under reflux for 4 h and finally cooled. Methanol (200 ml) was removed under nitrogen, glacial acetic acid (5 ml) added, and the mixture allowed to cool overnight. The precipitate of inorganic salts which had formed at this stage was filtered off (2.3 g). The filtrates were distilled to dryness, the resultant sticky solid was slurried in ether (100 ml), and the white suspension so obtained was chilled in ice. The solid was filtered off, dried, slurried in ice-cold water (100 ml) to remove inorganic salts, and isolated as before to give *sodium 5-hydroxy-3-methoxycarbonyl-7-t-butylbenzo*[b]*furan-2-olate* (4; R = Bu^t) (4.8 g, 32%), m.p. >300°; $\nu_{max.}$ 3 380 (OH) and 1 690 cm^{-1} (ester C=O); δ[$(CD_3)_2SO$] 1.32 (9 H, s, Bu^t), 3.64 (3 H, s, CO_2Me), 6.12 (1 H, d, *J* 2 Hz, ArH-6), and 6.68 (1 H, d, *J* 2 Hz, ArH-4).

Treatment with dilute hydrochloric acid,[1] as before, gave *5-hydroxy-3-methoxycarbonyl-7-t-butylbenzofuran-2(3H)-one* (6; R = Bu^t), which crystallised from methanol as needles, m.p. 156°; $\nu_{max.}$ 3 470 (OH), 1 825, 1 812 (lactone C=O), and 1 722 cm^{-1} (ester C=O); δ($CDCl_3$) 1.35 (9 H, s, Bu^t), 3.80 (3 H, s, CO_2Me), 4.60br (2 H, s, OH and OCH<), and 6.68—6.83 (2 H, distorted d, ArH) (Found: C, 63.8; H, 6.1%; M^+, 264. $C_{14}H_{16}O_5$ requires C, 63.6; H, 6.1%; *M*, 264).

Transformation of Dimethyl p*-Hydroxyphenoxymalonate* (8; R = H).—To dimethyl *p*-hydroxyphenoxymalonate (17 mg) in methanol (0.5 ml) was added, under nitrogen, methanolic sodium methoxide (1.6 ml of a 1% solution). A colour change from colourless to dark green resulted. After 2 h, the solvent was reduced to half bulk by passing a stream of nitrogen over the liquid; the solid so formed was filtered off, washed with methanol (3 ml), and oven-dried to give the product (5 mg, 31%). I.r. and ^1H n.m.r. spectra, together with t.l.c. comparison, showed the product to be sodium 5-hydroxy-3-methoxycarbonylbenzo[*b*]furan-2-olate (1; R = H).

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