Syntheses of Substituted 1,4-Naphthoquinones by Diels–Alder Addition of Methoxycyclohexadienes to Substituted 1,4-Benzoquinones

By **Robin G. F. Giles** * and **Gregory H. P. Roos**, Department of Organic Chemistry, University of Cape Town, South Africa 7700

Additions of 1-methoxycyclohexa-1,3-diene to 2-methoxy-3-methyl-1,4-benzoquinone and to chloro-1,4-benzoquinone give Diels–Alder adducts which are coverted in high yield into substituted juglone methyl ethers. Reactions between 1-methoxy-3-methylcyclohexa-1,3-diene and methoxy-1,4-benzoquinone follow a similar course. Addition of 1,3-dimethoxycyclohexa-1,3-diene to chloro- or methoxy-benzoquinone affords a dihydrodibenzofuran rather than a Diels–Alder adduct.

We have recently shown [1] that 1-methoxycyclohexa-1,3-diene (1) adds regiospecifically to 2-methoxy-1,4-benzoquinone (2); the Diels–Alder adduct (3) so formed can be converted in high yield into 3,5-dimethoxy-1,4-naphthoquinone (4). We report here some investigations aimed at determining the feasibility of using this type of reaction sequence to afford other appropriately substituted naphthoquinones.

Addition of the diene (1) to 2-methoxy-3-methyl-1,4-benzoquinone (5) would be of interest, as competition between the methoxy and methyl substituents of the latter would determine which plays the dominant role in the favoured transition state leading to the Diels–Alder adduct. One might anticipate that the methoxy should be more effective, giving the adduct (6) in preference to its isomer (7). The adduct (6) should then be convertible into the natural product droserone (15).

Addition of the diene (1) to the quinone (5) afforded a mixture of adducts (6) and (7) which proved difficult to separate; they were converted by enolisation with potassium t-butoxide and oxidation with silver oxide into the bridged quinones (8) and (9) [from which mixture small quantities of the major component (8) could be obtained pure by column chromatography] and thence into the naphthoquinones (10) and (11) by pyrolysis. The aromatic *O*-methyl groups were removed by treatment with boron tribromide in methylene chloride to afford the juglones (12) and (13).

The mixture of (12) and (13) was the most readily separated, and the components were shown to be present in the proportions *ca.* 4 : 1. This indicates that the adduct (6) is by far the major component in the initially formed mixture of adducts (6) and (7); *i.e.* the reaction shows considerable regioselectivity.

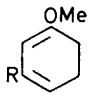
One might expect that the minor component (13) of the juglone mixture would possess the more effective intramolecular hydrogen bond between the *peri*-hydroxy and carbonyl groups through a resonance contribution from the canonical form (14). In fact compound (13) has a slightly higher R_F value, more strongly deshielded phenolic hydroxy (τ −2.20) and *O*-methyl groups (τ 5.85) [for (12), τ −1.74 and 5.90, respectively], and higher frequency non-bonded carbonyl (1 671 cm^{-1}), and lower frequency bonded carbonyl (1 632 cm^{-1}) absorptions [*cf.* 1 660 and 1 640 cm^{-1} for (12)].

Juglone (12) was converted into droserone (15) on stirring with dilute aqueous sodium hydroxide [m.p. 179—180° (lit.,[2] 181°)]. The m.p. of its diacetate (16) (118.5—119°) (lit.,[2] 119°) was not depressed on addition of the diacetate of the natural product. These m.p.s distinguish droserone from its isomer (17) [m.p. 190—

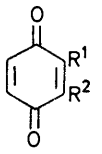
[1] R. G. F. Giles and G. H. P. Roos, *J.C.S. Perkin I*, 1976, 1632.

[2] M. Asano and J. Hase, *J. Pharm. Soc. Japan*, 1943, **63**, 83, 90 (*Chem. Abs.*, 1952, **46**, 92).

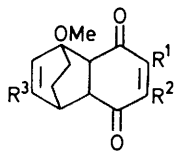
191° (decomp.); lit.,[2] 189—190°; diacetate (18), m.p. 157—159°; lit.,[2] 158—160°].



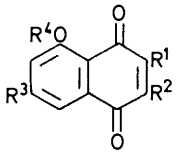
(1) R=H
(24) R=Me
(29) R=OMe



(2) R^1=OMe, R^2=H
(5) R^1=OMe, R^2=Me
(19) R^1=Cl, R^2=H

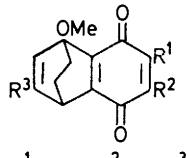


(3) R^1=OMe, R^2=R^3=H
(6) R^1=OMe, R^2=Me, R^3=H
(7) R^1=Me, R^2=OMe, R^3=H
(20) R^1=Cl, R^2=R^3=H
(25) R^1=OMe, R^2=H, R^3=Me
(31) R^1=R^3=OMe, R^2=H

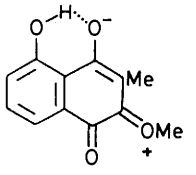


(4) R^1=OMe, R^2=R^3=H, R^4=Me
(10) R^1=OMe, R^2=R^4=Me, R^3=H
(11) R^1=R^4=Me, R^2=OMe, R^3=H
(12) R^1=OMe, R^2=Me, R^3=R^4=H
(13) R^1=Me, R^2=OMe, R^3=R^4=H
(15) R^1=OH, R^2=Me, R^3=R^4=H
(16) R^1=OAc, R^2=Me, R^3=H, R^4=Ac
(17) R^1=Me, R^2=OH, R^3=R^4=H
(18) R^1=Me, R^2=OAc, R^3=H, R^4=Ac
(22) R^1=Cl, R^2=R^3=H, R^4=Me
(23) R^1=Cl, R^2=R^3=R^4=H
(27) R^1=OMe, R^2=H, R^3=R^4=Me
(28) R^1=OMe, R^2=R^4=H, R^3=Me

Addition of methoxycyclohexadiene (1) to 2-chloro-1,4-benzoquinone (19) afforded an adduct (20) which was not isolated, but was converted into the quinone



(8) R^1=OMe, R^2=Me, R^3=H
(9) R^1=Me, R^2=OMe, R^3=H
(21) R^1=Cl, R^2=R^3=H
(26) R^1=OMe, R^2=H, R^3=Me

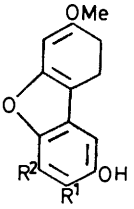


(14)

(21) as the sole product. This on heating gave 3-chloro-5-methoxy-1,4-naphthoquinone (22), which was identified by demethylation with boron trichloride to the known 3-chlorojuglone (23), m.p. 166—167° (lit.,[3] 166°). 2-Chlorojuglone has m.p. 112°.[4]

The reaction of 1-methoxy-3-methylcyclohexa-1,3-diene (24) with 2-methoxybenzoquinone (2) afforded the adduct (25) as the sole product, which was converted into the naphthoquinone (27) *via* the bridged species (26) as before. Demethylation with boron trichloride afforded 3-methoxy-7-methyljuglone (28), identical with an authentic sample.[5,6]

1,3-Dimethoxycyclohexa-1,3-diene (29) added to 2-methoxybenzoquinone to afford a white crystalline product, whose ^{1}H n.m.r. spectrum enabled the assignment of the dihydrodibenzofuran structure (30). This included two three-proton methoxy signals at τ 6.11 and 6.32 and two aromatic singlets at τ 3.07 and 3.18, the latter indicating a *para*-orientation of these protons. Two routes to the furan can be envisaged. One involves the initially formed adduct (31), which could rearrange to compound (30) by a mechanism put forward by Birch [7] for related Diels–Alder adducts. If this were so, formation of the adduct would have proceeded regiospecifically, as none of the alternative isomer (32) was observed. A second route to the furan (30) *via* nucleophilic attack by the diene on C-5 of the quinone could not be excluded since our attempts to isolate the postulated adduct (31) failed.



(30) R^1=OMe, R^2=H
(32) R^1=H, R^2=OMe
(33) R^1=Cl, R^2=H
(34) R^1=H, R^2=Cl

Finally, the reaction between the dimethoxy-diene (29) and chlorobenzoquinone (19) gave rise to the chlorodihydrodibenzofuran (33). Once again, two aromatic singlets in its ^{1}H n.m.r. spectrum excluded the isomeric structure (34).

EXPERIMENTAL

Unless otherwise stated i.r. spectra were measured for solutions in carbon tetrachloride and n.m.r. spectra for solutions in [^{2}H]chloroform with tetramethylsilane as internal reference. Column chromatography was carried out on dry columns with Merck Kieselgel 60 (70—230 mesh) or on Merck aluminium oxide (active; neutral). Light petroleum refers to the fraction, b.p. 60—80°.

2-Methoxy-3-methyl-1,4-benzoquinone.— 2,6-Dimethoxytoluene (5.45 g) in dry dimethylformamide (20 ml) was added at room temperature to a stirred solution of ethanethiol (7.1 g) in the same solvent (100 ml) containing sodium hydride (4.2 g of a 60% dispersion in oil). The solution was

[3] R. H. Thomson, *J. Chem. Soc.*, 1949, 1277.
[4] R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 377.
[5] (*a*) K. Yoshihira, M. Tezuka, C. Takahashi, and S. Natori, *Chem. and Pharm. Bull. (Japan)*, 1971, **19**, 851; (*b*) M. Tezuka, M. Kuroyanagi, K. Yoshihira, and S. Natori, *ibid.*, 1972, **20**, 2029.
[6] R. G. F. Giles and G. H. P. Roos, *Tetrahedron Letters*, 1975, 4159.
[7] A. J. Birch, D. N. Butler, and J. B. Siddall, *J. Chem. Soc.*, 1964, 2932.

heated under reflux for 2 h, and then worked up according to the procedure of Mirrington [8] for the demethylation of anisoles, to give 3-methoxy-2-methylphenol (4.8 g, 99%). This was oxidised to 2-methoxy-3-methyl-1,4-benzoquinone with Fremy's salt.[9]

1,4-Dihydro-1,7-dimethoxy-6-methyl-1,4-ethano-5,8-naphthoquinone (8) *and* *1,4-Dihydro-1,6-dimethoxy-7-methyl-1,4-ethano-5,8-naphthoquinone* (9).—The quinone (5) (1.85 g) in benzene (150 ml) was treated with the diene (1) (4.2 g) containing about 30% of the isomeric 1,4-diene.[10] The solution was heated under reflux for 1.5 h, after which t.l.c. indicated consumption of all the quinone (5). The solvent was evaporated off and the pale orange residue chromatographed over a neutral alumina column. This was eluted with benzene to remove the excess of diene, then with 20% ethyl acetate in benzene to afford the adduct mixture as an oil. This was dissolved in dry tetrahydrofuran (40 ml) and an excess of potassium t-butoxide (2.5 g) was added. The mixture was stirred for 1 h, and then diluted with water (40 ml) and made just acidic with dilute hydrochloric acid. It was then extracted with ether and the extract was washed exhaustively with water to remove the excess of tetrahydrofuran, dried, and treated with an excess of silver(I) oxide (5 g). The resulting mixture was stirred for 3 h, filtered, dried, and evaporated. The residue was chromatographed over a short silica column (5% ethyl acetate–benzene). This yielded the quinone mixture [2.8 g, 86% based on quinone (5)], as a partially crystalline orange oil. T.l.c. indicated two overlapping constituents (Found: C, 69.2; H, 6.4. Calc. for $C_{15}H_{16}O_4$: C, 69.2; H, 6.15%), $\nu_{max.}$ (neat) 1 665, 1 645, 1 615, and 1 589 cm^{-1}, τ 3.44 (1 H, dd, J 8 and 1 Hz, 2-H), 3.67 (1 H, dd, J 8 and 6 Hz, 3-H), 5.7 (1 H, m, bridgehead H), 6.01 (3 H, s, OCH_3), 6.16 (3 H, s, OCH_3), 8.08 (3 H, s, CCH_3), 8.1—8.8 (4 H, m, $CH_2{\cdot}CH_2$). Chromatography of a separate sample over a silica column with 5% ethyl acetate–light petroleum afforded later fractions which contained pure bridged *quinone* (8), with analytical and n.m.r. spectral data as above.

3,5-Dimethoxy-2-methyl-1,4-naphthoquinone (10) *and* *2,5-methoxy-3-methyl-1,4-naphthoquinone* (11).—The foregoing mixture (2.7 g) was heated at 115 °C (bath) and 8 mmHg, under which conditions bubbling occurred as ethylene was eliminated. When bubbling ceased, by which time the oil had crystallised, sublimation at 140 °C and 0.5 mmHg afforded the light yellow naphthoquinone mixture (2.23 g, 94%). Preparative t.l.c. (eluant 50% chloroform–light petroleum) gave a sample (Found: C, 67.4; H, 5.1. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.2%), τ 2.22—2.52 (2 H, m, 7- and 8-H), 2.78br (1 H, d, J 8 Hz, 6-H), 5.90 and 6.01 (major component) and 5.95 and 6.01 (minor component) (6 H, all singlets, OCH_3), and 7.94 (minor) and 7.97 (major) (3 H, singlets, CCH_3).

3,5-Dimethoxy-2-methyl-1,4-naphthoquinone (10).—The *quinone* (10) was prepared as above from the pure bridged quinone (8); m.p. 111—112° (Found: C, 67.4; H, 5.2. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.2%), τ 2.28 (1 H, dd, J 8 and 2 Hz, 8-H), 2.41 (1 H, t, J 8 Hz, 7-H), 2.78 (1 H, dd, J 8 and 2 Hz, 6-H), 5.90 (3 H, s, OCH_3), 6.01 (3 H, s, OCH_3), and 7.97 (3 H, s, CCH_3).

5-Hydroxy-3-methoxy-2-methyl-1,4-naphthoquinone (12) *and* *5-Hydroxy-2-methoxy-3-methyl-1,4-naphthoquinone* (13).—The mixture of quinones (10) and (11) (100 mg) was stirred at −78 °C in methylene chloride (10 ml), and boron tribromide (140 mg, 1.2 mol. equiv.) was added in methylene chloride (10 ml). After 10 min, the mixture was allowed to warm to room temperature, thrown into water, and extracted with methylene chloride. The organic layer was dried and evaporated. The solid residue was chromatographed (preparative t.l.c.; eluant 5% ethyl acetate–light petroleum) to give, in the band of highest R_F, the *quinone* (13) as orange needles (15 mg, 16%), m.p. 127.5—128° (light petroleum) (Found: C, 66.1; H, 4.7. $C_{12}H_{10}O_4$ requires C, 66.05; H, 4.6%), $\nu_{max.}$ 1 671 and 1 632 cm^{-1}, τ −2.20 (1 H, s, OH), 2.16—2.90 (3 H, m, 6-, 7-, and 8-H), 5.85 (3 H, s, OCH_3), and 7.93 (3 H, s, CCH_3). A second band afforded the *quinone* (12) as yellow needles (60 mg, 64%), m.p. 107.5—109° (light petroleum) (Found: C, 65.75; H, 4.7%), $\nu_{max.}$ 1 660 and 1 640 cm^{-1}, τ −1.74 (1 H, s, OH), 2.15—2.97 (3 H, m, 6-, 7-, and 8-H), 5.90 (3 H, s, OCH_3), and 7.92 (3 H, s, CCH_3).

Droserone [*3,5-Dihydroxy-2-methyl-1,4-naphthoquinone*] (15).—The quinone (12) (80 mg) was stirred with sodium hydroxide (5%; 10 ml) until all starting material had dissolved. The solution was washed with ether, acidified, and extracted with chloroform. The organic layer was dried and evaporated and the residue chromatographed (preparative t.l.c.; 10% ethyl acetate–light petroleum) to give *droserone* (75 mg), m.p. 179—180° (from methylene chloride–light petroleum) (Found: C, 65.0; H, 4.3. $C_{11}H_8O_4$ requires C, 64.7; H, 3.9%), $\nu_{max.}$ ($CHCl_3$) 3 445, 1 650, and 1 628 cm^{-1}, τ −1.08 (1 H, s, bonded OH), 2.06—2.90 (3 H, m, 6-, 7-, and 8-H), 2.36 (1 H, s, quinonoid OH), and 7.90 (3 H, s, CH_3); the dicaetate (16) (made with pyridine–acetic anhydride) had m.p. 118.5—119°, τ 1.94 (1 H, d, J 8 Hz, 8-H), 2.30 (1 H, t, J 8 Hz, 7-H), 2.65 (1 H, d, J 8 Hz, 6-H), 7.56 (3 H, s, Ac), 7.60 (3 H, s, Ac), and 7.92 (3 H, s, quinonoid CH_3).

2,5-Dihydroxy-3-methyl-1,4-naphthoquinone (17).—The quinone (13) (75 mg) was treated as for its isomer (12). Work-up as before gave the quinone (17) (55 mg, 77%), m.p. 190—191° (decomp.), τ −2.39 (1 H, s, bonded OH), 2.30—2.84 (4 H, m, 6-, 7- and 8-H, and quinonoid OH), and 7.91 (3 H, s, CH_3); the diacetate (18) had m.p. 157—159°, τ 1.96 (1 H, d, J 8 Hz, 8-H), 2.32 (1 H, t, J 8 Hz, 7-H), 2.66 (1 H, d, J 8 Hz, 6-H), 7.55 (3 H, s, Ac), 7.61 (3 H, s, Ac), and 7.95 (3 H, s, quinonoid CH_3).

7-Chloro-1,4-dihydro-1-methoxy-1,4-ethano-5,8-naphthoquinone (21).—Chlorobenzoquinone (5 g) and an excess of the diene (1) (7.5 g) (containing about 30% of the isomeric diene) were stirred in benzene (100 ml) at room temperature until all the quinone had been consumed (as indicated by t.l.c.) (*ca.* 2 h). The solvent was evaporated off and the residue dissolved in dry tetrahydrofuran (100 ml) to which an excess of potassium t-butoxide (8 g) was added. The solution was stirred for 1 h, and then acidified, and the product was oxidised with silver(I) oxide as before. The crude product was chromatographed over silica (10% ethyl acetate–light petroleum) to give the orange *quinone* as an oil (2.58 g, 30%) (Found: C, 62.1; H, 4.7. $C_{13}H_{11}ClO_3$ requires C, 62.3; H, 4.4%), $\nu_{max.}$ (neat) 1 678 and 1 650 cm^{-1}, τ 3.14 (1 H, s, quinonoid H), 3.41 (1 H, dd, J 8 and 1 Hz, 2-H), 3.69 (1 H, dd, J 8 and 6 Hz, 3-H), 5.7 (1 H, m, bridgehead H), 6.37 (3 H, s, OCH_3), and 8.0—8.9 (4 H, m, $CH_2{\cdot}CH_2$).

3-Chloro-5-methoxy-1,4-naphthoquinone (22).—Prepared as

[8] G. I. Feutrill and R. N. Mirrington, *Austral. J. Chem.*, 1972, **25**, 1719.

[9] A. Rashid and G. Read, *J. Chem. Soc.* (*C*), 1967, 1323.

[10] A. J. Birch and K. P. Dastur, *J.C.S. Perkin I*, 1973, 1650.

described earlier for the quinones (10) and (11), the *product* (22) sublimed at 130 °C and 1.5 mmHg in quantitative yield; m.p. 159—160.5° (Found: C, 59.5; H, 3.5. $C_{11}H_7ClO_3$ requires C, 59.35; H, 3.2%), $\nu_{max.}$ ($CHCl_3$) 1 680, 1 668, and 1 610 cm^{-1}, τ 2.3—2.9 (3 H, m, 6-, 7-, and 8-H), 2.90 (1 H, s, quinonoid H), and 6.00 (3 H, s, OCH_3).

3-*Chloro*-5-*hydroxy*-1,4-*naphthoquinone* (23).—The quinone (22) (100 mg) in dry methylene chloride (10 ml) was treated at −78 °C with boron trichloride (48 mg, 1 mol equiv.) in methylene chloride (10 ml). After work-up, the residue was chromatographed over a short silica column to afford the product (55 mg, 83% based on starting material consumed), which was sublimed [100—105 °C (bath) and 0.6 mmHg]; m.p. 166—167°, τ −1.77 (1 H, s, OH), 2.1—2.9 (3 H, m, 6-, 7-, and 8-H), and 2.83 (1 H, s, quinonoid H). Further elution provided starting material (35 mg).

1,4,4a,8a-*Tetrahydro*-1,7-*dimethoxy*-3-*methyl*-1,4-*ethano*-5,8-*naphthoquinone* (25).—The diene (24) (2.9 g), prepared by Birch's dichloromaleic anhydride isomerisation of its 1,4-isomer,[10] was added to a solution of methoxybenzoquinone (2) (1.7 g) in benzene (50 ml). The mixture was heated under reflux for 4 h. The solvent was evaporated off, and the residue chromatographed over a silica column (eluant 30% ethyl acetate–light petroleum) to yield the *adduct* (2.6 g, 81%), m.p. 111.5—112.5° (from benzene–light petroleum) (Found: C, 68.7; H, 6.8. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%), $\nu_{max.}$ (Nujol) 1 690, 1 647, and 1 610 cm^{-1}, τ 4.12 (1 H, s, 6-H), 4.26br (1 H, s, 2-H), 6.27 (3 H, s, OCH_3), 6.58 (3 H, s, OCH_3), 6.70 (1 H, d, J 8 Hz, 8a-H), 6.95 (1 H, dd, J 8 and 3 Hz, 4a-H), 7.09br (1 H, s, 4-H), 7.9—8.8 (4 H, m, $CH_2{\cdot}CH_2$), 8.26 (3 H, s, CCH_3).

1,4-*Dihydro*-1,7-*dimethoxy*-3-*methyl*-1,4-*ethano*-5,8-*naphthoquinone* (26).—The foregoing adduct (220 mg) was enolised as before with potassium t-butoxide (400 mg). Work-up and oxidation in the usual way with silver(I) oxide (1 g) afforded the product, which was chromatographed over a short silica column (eluant chloroform) to give the *quinone* (205 mg, 92%), m.p. 124—126° (Found: C, 69.3; H, 6.3. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.1%), $\nu_{max.}$ (Nujol) 1 675, 1 630, and 1 584 cm^{-1}, τ 3.93br (1 H, s, 2-H), 4.23 (1 H, d, 6-H), 5.96br (1 H, s, 4-H), 6.18 (3 H, s, OCH_3), 6.42 (3 H, s, OCH_3), 7.95—8.8 (4 H, m, $CH_2{\cdot}CH_2$), 8.10 (3 H, s, CCH_3).

3,5-*Dimethoxy*-7-*methyl*-1,4-*naphthoquinone* (27).—The foregoing quinone was aromatised as described earlier; the *product* (92%) had m.p. 174—176° (Found: C, 66.9; H, 5.3. $C_{13}H_{12}O_4$ requires C, 67.2; H, 5.2%), $\nu_{max.}$ (Nujol) 1 678, 1 655, and 1 621 cm^{-1}, τ 2.47 (1 H, s, 8-H), 2.96 (1 H, s, 6-H), 3.96 (1 H, s, 2-H), 6.01 (3 H, s, OCH_3), 6.13 (3 H, s, OCH_3), and 7.53 (3 H, s, CCH_3).

5-*Hydroxy*-3-*methoxy*-7-*methyl*-1,4-*naphthoquinone* (28).—The quinone (27) (100 mg) in methylene chloride (6 ml) was treated with boron trichloride (100 mg) in the same solvent at −10 °C. The solution was stirred at that temperature for 30 min and then allowed to warm to room temperature. Work-up in the usual way gave the product in an almost pure state. A sample prepared by chromatography over a short column (eluant 10% ethyl acetate–light petroleum) (yield 87 mg, 92%) had m.p. and mixed m.p. 209—210° (lit.,[5] 209—210°) (Found: C, 66.2; H, 4.7. Calc. for $C_{12}H_{10}O_4$: C, 66.1; H, 4.6%).

8,9-*Dihydro*-3,7-*dimethoxydibenzofuran*-2-*ol* (30).—2-Methoxybenzoquinone (2 g) and the diene (29) (4 g of a mixture containing about 33% of the 1,4-isomer) were heated under reflux for 3 h. The solvent was evaporated off and the product chromatographed over either an alumina or a silica column with benzene to give the white *product* (2.4 g, 67%), m.p. 179—180° (from methylene chloride–light petroleum) (Found: C, 68.5; H, 5.8. $C_{14}H_{14}O_4$ requires C, 68.3; H, 5.7%), $\nu_{max.}$ (Nujol) 3 440 cm^{-1}, τ 3.07 and 3.18 (1 H, each, s, 1- and 4-H), 4.51br (2 H, s, 6-H and OH; the latter exchanges with D_2O), 6.11 (3 H, s, OCH_3), 6.31 (3 H, s, OCH_3), and 7.0—7.6 (4 H, m, CH_2CH_2). The same reaction occurred at room temperature and at 0 °C.

3-*Chloro*-8,9-*dihydro*-7-*methoxydibenzofuran*-2-*ol* (33).—Chlorobenzoquinone (19) (1 g) and the diene (29) (2 g) were stirred together in benzene (50 ml) at room temperature for 20 min. The solvent was removed and the product chromatographed over a short column (10% ethyl acetate–light petroleum) to afford the white *product* (0.6 g, 34%), m.p. 115—116° (from methylene chloride–light petroleum) (Found: C, 62.5; H, 4.7. $C_{13}H_{11}ClO_3$ requires C, 62.3; H, 4.4%), τ 2.72 (1 H, s, 4-H), 3.14 (1 H, s, 1-H), 4.54 (1 H, s, OH, D_2O-exchangeable), 4.64 (1 H, s, 6-H), 6.32 (3 H, s, OCH_3), and 7.0—7.6 (4 H, m, $CH_2{\cdot}CH_2$).

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