Spirans. Part 11.[1] A New Method for Generating *o*-Quinone Methides, and its Applications to the Synthesis of Spirochromans. A Note on the Autoxidation of a Naphthol Derivative

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The adducts (5) and (9) formed from quinonyl carbanions and tetramethyl-1,4-benzoquinone are reduced by zinc in acetic acid giving the component phenols. It is considered that *o*-quinone methides are intermediates, aromatisation of the quinonoid ring being the driving force (Scheme 1). The corresponding ethers (6), (7), and (10) give *o*-quinone methides that are either readily trapped by acetate ion giving phenolic benzyl acetates (13) and (17) or dimerise giving the bisnaphthol (25) *via* the spiran (24). The benzylic acetates form excellent substrates for conversion into spirans such as (4) by standard methods; the spiran (24) can be regenerated from the bisnaphthol by oxidative cyclisation.

The naphthol derivative (23) obtained as a by-product is rapidly oxidised by air to give the hydroperoxide (26).

THE oxidation of tocopherol and related chromans (1) produces *o*-quinone methides (2) that rapidly dimerise to the spirans [2] (3). These have unusual properties, behaving as fluxional molecules and being sensitive to reduction by ascorbic acid.[3] In order to obtain information as to what extent such properties are determined by substitution patterns and/or ring fusions we have prepared several related compounds. We describe here a new method for generating *o*-quinone methides and its application to the synthesis of the spiran (4) and two others.

The xanthen derivative (5), ' diduroquinone,' is very easily obtained by treating duroquinone (8) with alkali; [4] one molecule of quinone forms a carbanion that appears to undergo a cycloaddition to a second.[4-6] Smith, Tess, and Ullyot [4] studied the reduction of this xanthen with zinc in acetic acid and obtained tetramethylquinol as the sole product. Various methods of reduction failed to produce any useful result when applied to the ethyl ether of the xanthen. In our earlier work we caused a naphthoquinonyl carbanion to add to duroquinone (8) giving the xanthen derivative (9), and found that zinc and acetic acid reduced it to tetramethylquinol and 2,3-dimethylnaphthalene-1,4-diol.[6] Evidently both xanthens are cleaved across the heterocycle. A stepwise mechanism was suggested originally,[6] but while the reduction of ether links adjacent to carbonyl groups is well known, a similar cleavage of carbon–carbon links is rare and does not seem to have been observed for zinc reductions. We therefore prefer to regard the cleavage as initiated by reduction of the enedione grouping (Scheme 1) followed by (or perhaps synchronous with) an electrocyclic reversion to quinol (from ring B) and quinone methide (from ring A). If the starting material is the phenol (5), then the quinone methide (11) can tautomerise to a quinone and will therefore also give tetramethylquinol. This accounts for the observations made by Smith *et al.*[4] and by us.[6] It is clear, however, that if the starting material is the ether (6), the fate of the quinone methide would be modified. In fact, and in contrast to the report by Smith *et al.*,[4] the reduction of the methyl ether gave the benzylic acetate (13), derived by the nucleophilic addition of acetate ion to (12) (Scheme 1). We therefore hoped that, by withholding nucleophiles, we would allow the quinone methide (12) time enough to dimerise to the desired spiran (4), but zinc and trifluoroacetic acid merely reduced it to the quinol derivative (14).

[1] Part 10, A. W. Dick, F. M. Dean, D. A. Matkin, and M. L. Robinson, *J.C.S. Perkin I*, 1977, 2204.

[2] D. R. Nelan and C. D. Robeson, *J. Amer. Chem. Soc.*, 1962, **84**, 2963; P. Schudel, H. Mayer, J. Metzger, R. Ruegg, and O. Isler, *Helv. Chim. Acta*, 1963, **46**, 636; D. McHale and J. Green, *Chem. and Ind.*, 1964, 366; J. L. G. Nilsson, *Acta Pharm. Suecica*, 1969, **6**, 1; J. L. G. Nilsson, J.-O. Bransted, and H. Sievertsson, *ibid.*, 1968, **5**, 509.

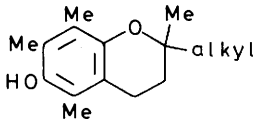
[3] H. A. Lloyd, E. A. Sokoloski, B. S. Strauch, and H. M. Fales, *Chem. Comm.*, 1969, 299; W. A. Skinner and P. A. Alaupovic, *J. Org. Chem.*, 1963, **28**, 2854; M. S. Chauhan, F. M. Dean, and M. L. Robinson, *Chem. Comm.*, 1971, 1141.

[4] L. I. Smith, R. W. H. Tess, and G. E. Ullyot, *J. Amer. Chem. Soc.*, 1944, **66**, 1320.

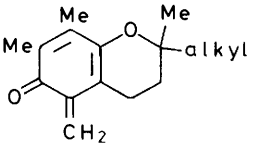
[5] K. Chandrasenan and R. H. Thomson, *J. Chem. Soc.* (*C*), 1966, 123.

[6] F. M. Dean and L. E. Houghton, *J. Chem. Soc.* (*C*), 1968, 1060.

Fortunately, the benzylic acetate (13) is itself a suitable starting material for quinone methide production. When heated in mesitylene (or in the mass spectrometer) it rapidly collapsed by loss of acetic acid to form (12), which then gave the trimer corresponding to the addition of a third quinone methide molecule to the



(1)



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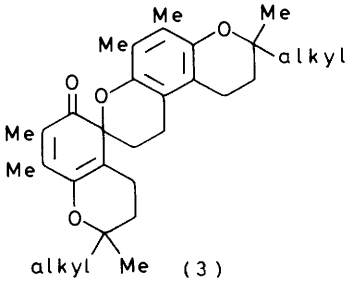

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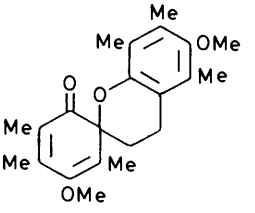

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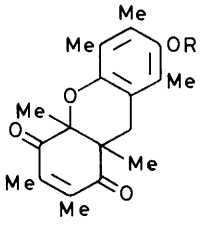
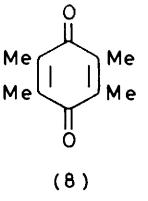
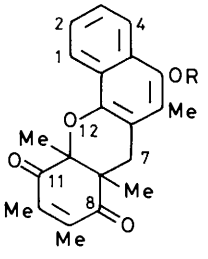


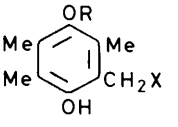
(5) R = H
(6) R = Me
(7) R = Me_2CH



(8)

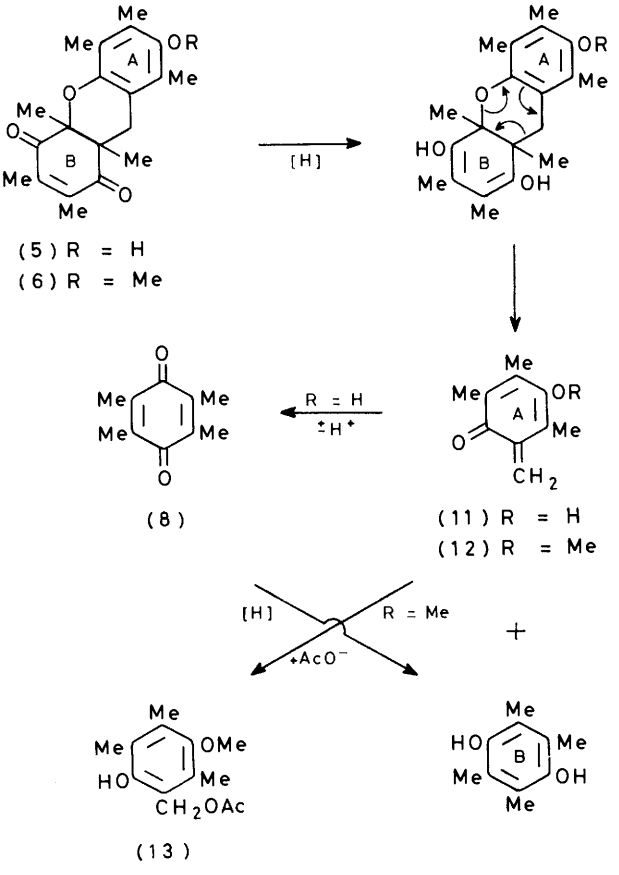


(9) R = H
(10) R = Me



(13) R = Me, X = OAc
(14) R = Me, X = H
(15) R = Me, X = OH
(16) R = Me, X = Cl
(17) R = Me_2CH, X = OAc
(18) R = Me_2CH, X = OH
(19) R = Me_2CH, X = Cl

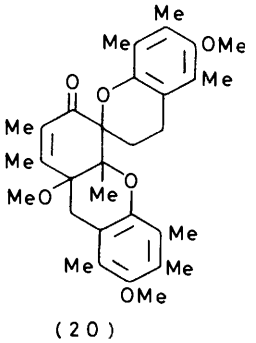
spiro-dimer (4). This trimer is (very tentatively) assigned structure (20) on the basis of analogy and consistent n.m.r. and other spectroscopic results.[7,8] *trans*-Stilbene trapped the quinone methide as the chroman derivative (21). Since spirans can themselves dissociate into quinone methides, higher temperatures favour trimer formation,[8,9] so a low temperature reaction was investigated. Reduction of the benzyl acetate with lithium



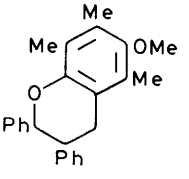
(5) R = H
(6) R = Me
(8)
(11) R = H
(12) R = Me
(13)

SCHEME 1

aluminium hydride gave the alcohol (15), and sudden treatment with hydrogen chloride converted this into the halide (16). Nucleophilic displacement with sodium



(20)



(21)

hydrogen carbonate gave the yellow quinone methide (12) which dimerised almost at once to the desired spiran (4).

In the same way the xanthen (5) was converted into

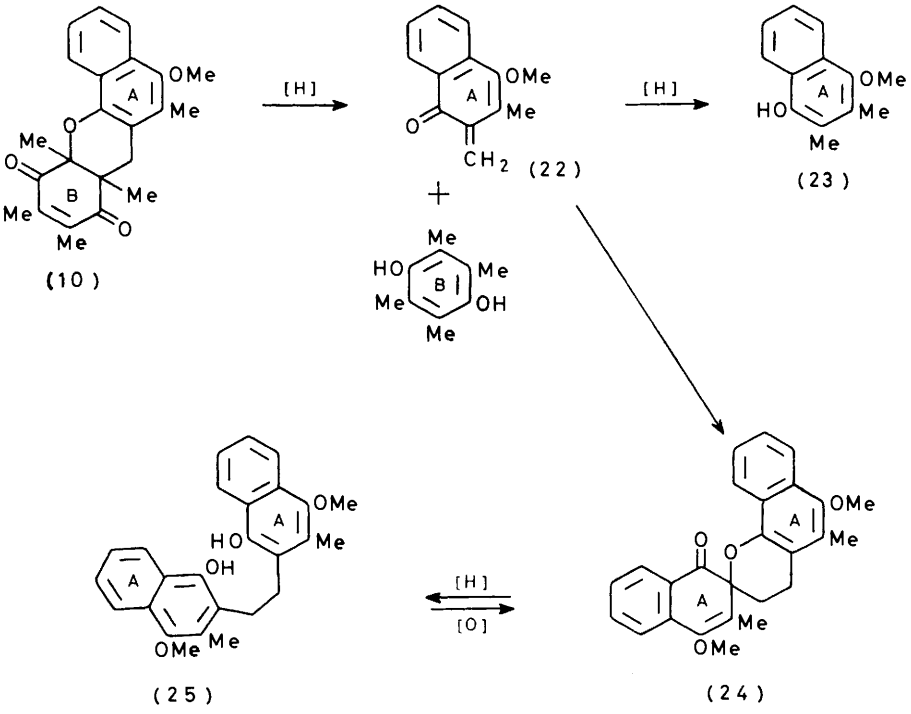
[7] S. B. Cavitt, H. Sarrafizadeh, R. Gardner, and P. D. Gardner, *J. Org. Chem.*, 1962, **27**, 1211; A. Merijan, B. A. Shoulders, and P. D. Gardner, *ibid.*, 1963, **28**, 2148.

[8] Part 9, M. S. Chauhan, F. M. Dean, S. McDonald, and M. L. Robinson, *J.C.S. Perkin I*, 1973, 319.

[9] Part 8, M. S. Chauhan, F. M. Dean, D. Matkin, and M. L. Robinson, *J.C.S. Perkin I*, 1973, 120.

the isopropyl ether (7), which was carried through the sequence terminating in the halide (19). Treatment with base again gave the desired spiran (4; Me_2CHO for MeO). During the conversion of the alcohol (18) into the halide (19) there seemed to be little loss caused by acid-catalysed removal of the isopropyl group. In contrast, this loss dominated the pyrolysis of the acetate (17) in mesitylene, for instead of a dimer or trimer the sole product was duroquinone (8); evidently the quinone methide (11) and isopropyl acetate are formed, but in the absence of a nucleophile or a reducing agent, tautomerism as in the Scheme leads to the quinone and there is no further reaction.

A somewhat different result attended the reduction of the naphthalene derivative (10) with zinc. Tetramethylquinol was formed as before, but the quinone methide (22) appeared to be partitioned between two sequences, one terminating in the naphthol (23) and the other in the bisnaphthol (25) (Scheme 2).



SCHEME 2

Thus the naphthoquinone methide dimerises but does not add acetate, while the benzoquinone methide adds acetate but does not dimerise. This marked difference could arise from the relative aromatic stabilisation energies, restitution of aromaticity being less important for the naphthalene than for the benzene system. Hence the naphthoquinone methide (22) must be a relatively stable one capable of surviving long enough to dimerise in the reaction medium giving the spiran (24). Indeed, this is the desired spiran, but suffers reduction by zinc to the bisnaphthol. It is readily regenerated by oxidation of the bisnaphthol with hexacyanoferrate(III) (Scheme 2). Under the same conditions the benzoquinone methide will tend to make an early capture of any nucleophile provided. In the reaction in trifluoroacetic acid it aromatised by reduction before it had time to dimerise.

Quinone methides have been generated by oxidation [10] and several other techniques [11] but not previously by reductive methods. The new method also offers a simple means of procuring selective asymmetric substitution patterns in quinol derivatives when only symmetrical precursors are available. An alternative and more general solution to this problem has been described recently but requires facilities for anodic oxidation.[12]

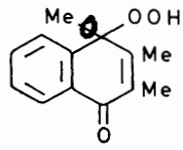
Note on the Naphthol (23).—Solutions of this compound in hydrocarbons proved difficult to handle because of an unusually rapid reaction with air. For this reason the compound was isolated and characterised as the acetate. Left in air, the naphthol itself changed into a compound assigned structure (26) mainly on spectroscopic grounds. The i.r. spectrum indicated hydroxylic and double conjugated carbonyl functions; the n.m.r. spectrum indicated two vinylic methyl groups (subject to slight long-range coupling) together with a methoxy methyl group resonating at rather high fields because it has to rotate through the shielding cone of the benzene ring. In 2-naphthol derivatives, hydroperoxidation has been associated with steric hindrance to planarity of the aromatic

[10] D. A. Bolon, *J. Org. Chem.*, 1970, **35**, 715, 3666.

[11] A. B. Turner, *Quart. Rev.*, 1964, **18**, 347; D. Creed, *J.C.S. Chem. Comm.*, 1976, 121; W. W. Sullivan, D. Ullman, and H. Schechter, *Tetrahedron Letters*, 1969, 457.

[12] M. J. Manning, D. R. Henton, and J. S. Swenton, *Tetrahedron Letters*, 1977, 1679.

ring induced by a single large substituent such as t-butyl.[13] The present case is essentially similar. Four serried



(26)

substituents must tend to buckle a ring already of relatively low aromaticity thus promoting the change to sp^3 hybridisation at one position.

EXPERIMENTAL

I.r. spectra were normally determined on mulls in paraffin; only the strongest bands are noted. U.v. spectra were determined upon ethanolic 10^{-3}—10^{-4}M-solutions. N.m.r. spectra given in the text were recorded under the same conditions as those in the Tables. Mass spectra were measured at about 70 eV with a source temperature near 200 °C; *m/e* values for molecular ions only are noted. Light petroleum had b.p. 60—80 °C.

TABLE 1

^{1}H N.m.r. spectra (τ scale)[a] of polycyclic quinol derivatives (in $CDCl_3$ at 100 MHz)

	Compound				
Assignment	(6)	(7)	(4)	(4; Pr^iO for MeO)[b]	(21)[c]
$ArOCH_3$	6.46		6.39		6.37
Vinyl OCH_3			6.45		
Me_2CHO		6.06—6.28		6.10—6.34	
CH_AH_B	7.08[d] 7.64[d]	6.88[d] 7.68[d]			
$CH{\cdot}CH_2$					*ca.* 7.0[e]
$PhCH{\cdot}O$					5.05[f]
$ArCH_3$	7.86	7.82	7.80	7.96	7.78
$ArCH_3$	7.91	7.91	7.88	7.96	7.85
$ArCH_3$	7.99	7.99	7.88	8.06	7.87
Vinyl CH_3	8.03	8.35	7.98	8.29	
Vinyl CH_3	8.03	8.35	8.06	8.29	
Vinyl CH_3			8.14	8.29	
$ArCH_2{\cdot}CH_2$			7.43—7.73	7.60—7.88	
$ArCH_2{\cdot}CH_2$			7.95—8.25[g]	8.00 8.30[g]	
$CH_3C(O{\cdot})(CO{\cdot})$	8.60	8.72			
$CH_3C(CH_2{\cdot})(CO{\cdot})$	8.79	8.90			
$(CH_3)_2CH$		8.91[h]		9.0[e]	

[a] Coupling constants in Hz. All bands had the appropriate relative intensities. [b] In chlorobenzene. [c] ArH; complex overlapping multiplets near τ 3. [d] *J* 17 Hz. [e] Ill resolved multiplet. [f] *J* 8 Hz. [g] Partially obscured by other bands. [h] *J* 6 Hz.

(7a*R*,* 11a*S* *)-7a,11a-*Dihydro*-5-*hydroxy*-6,7a,9,10,11a-*pentamethyl*-7H-*benzo*[a]*xanthen*-8,11-*dione* (9).—The following method gave a superior yield to that described previously The requisite tetrahydroindazole (3.0 g), dissolved in trichloromethane (34 ml) and methanol (135 ml), was added dropwise during 2 h to tetramethyl-1,4-benzoquinone (9.1 g; *i.e.* a large excess) and sodium acetate trihydrate (2.2 g) in methanol (330 ml) stirred under nitrogen. After 1 h more the mixture was cooled to 0 °C and the orange precipitate removed, washed with cold methanol, and crystallised from benzene–trichloromethane to give the xanthendione as orange needles (4.14 g, 85%), m.p. 220°. The excess of the tetramethylbenzoquinone was readily retrieved from the solutions and purified for repeated use.

TABLE 2

^{1}H N.m.r. spectra (τ scale) of simple quinol derivatives (in $CDCl_3$ at 100 MHz)[a]

	Compound						
Assignment	(13)	(14)	(15)	(16)	(17)	(18)	(19)
$ArCH_2X$	5.16		5.18[b]	5.26	5.16	5.26[b]	5.19
MeO	6.66	6.64	6.42	6.39	6.20[c]	6.10[c]	6.06[c]
$ArCH_3$	7.78	7.90	7.81	7.68	7.78	7.86	7.72
$ArCH_3$	7.78	7.90	7.86	7.78	7.78	7.90	7.84
$ArCH_3$	7.92	8.08	7.91		7.94	8.06	7.88
$ArCH_3$		8.08					
$(CH_3)_2CH$					8.91[d]	8.78[d]	8.75[d]
Me_2CH					6.20[e]	6.10[e]	6.06[e]
AcO	8.58				8.64		
ArOH			2.34[f,g]			2.30[f,g]	
CH_2OH			7.34[g,h]			7.04[g,h]	

[a] Coupling constants in Hz. All bands had the appropriate relative intensities. [b] Broad; sharp after contact with D_2O. [c] Me_2CHO; septet. [d] d, *J* 6 Hz. [e] m, *J* 6 Hz. [f] Relatively sharp; H-bonded. [g] Removed by D_2O. [h] Very broad.

The *methyl ether* (10) was obtained from the xanthendione (3.0 g) by treatment with dimethyl sulphate (1 ml) and potassium carbonate (20 g) in refluxing acetone (150 ml) for 4 h, and formed yellow needles (from benzene–light petroleum) (2.8 g), m.p. 161.5—162.5°, $\nu_{max.}$ 1 675 cm^{-1} (conj. C : O) (Found: C, 75.8; H, 6.55%; M^+, 364. $C_{23}H_{24}O_4$ requires C, 75.8; H, 6.6%; *M*, 364).

Reduction of the Xanthendione (10) *by Zinc.*—Zinc dust (10 g) was slowly stirred into a solution of the methoxyxanthendione (10) (1.0 g) in acetic acid (20 ml) heated on a steam-bath. After about 20 min. the mixture became colourless and was filtered hot. The residue was extracted with a little hot acetic acid; the combined solutions on cooling gave a crystalline mass of tetramethylquinone (280 mg). The mother liquor was poured into brine (100 ml) and kept at 0 °C under carbon dioxide for 2 h. A pink solid separated which was washed with water, dried *in vacuo* (P_2O_5), and purified from benzene–light petroleum to give 4,4′-*dimethoxy*-3,3′-*dimethyl*-2,2′-*ethylenebis*-1-*naphthol* (25) as plates (*ca.* 180 mg), m.p. 206°, $\nu_{max.}$ 3 400br, 1 592, 1 360, and 765 cm^{-1} (Found: C, 77.3; H, 6.4%; M^+, 402. $C_{26}H_{26}O_4$ requires C, 77.6; H, 6.5%; *M*, 402.)

The benzene–light petroleum mother liquors contained 4-methoxy-2,3-dimethyl-1-naphthol (22) but this deteriorated when attempts were made to isolate it. In another experiment, these liquors were concentrated *in vacuo*, the oily residue was treated with acetic anhydride and pyridine, and the product was chromatographed on silica with benzene. The chief fraction was an oil that slowly crystallised from benzene, giving 4-*methoxy*-2,3-*dimethyl*-1-*naphthyl acetate* as needles, m.p. 55°, $\nu_{max.}$ 1 745, 1 350, 1 226, 1 081, 1 025, and 761 cm^{-1} (Found: C, 73.8; H, 6.8%; M^+, 224. $C_{15}H_{16}O_3$ requires C, 73.75; H, 6.6%; *M*, 244).

In a third experiment the benzene–light petroleum mother liquors were left in air to allow the deterioration to continue. During 30 h a solid (130 mg) separated which readily crystallised from ether–light petroleum giving 4-*hydroperoxy*-4-*methoxy*-2,3-*dimethylnaphthalen*-1(4H)-*one* (26) as needles,

[13] P. A. Brady and J. Carnduff, *J.C.S. Chem. Comm.*, 1974, 816.

m.p. 122°, $\nu_{max.}$ 3 350 and 1 655 cm^{-2} (Found: M^+, 234.0886. $C_{13}H_{14}O_4$ requires M, 234.0920).

3,4-Dihydro-4',6-dimethoxy-3',5-dimethyl-2H-benzo[h]-*chromen-2-spiro-2'-naphthalen-1'-one* (24).—The ethylene bisnaphthol (25) (100 mg) in benzene (20 ml) was slowly added to a stirred solution of potassium hexacyanoferrate(III) (1.0 g) in water (20 ml), and after 1 h the benzene layer was separated, washed with water, and dried (Na_2CO_4). The material left after evaporation was chromatographed on silica from benzene–trichloromethane (1 : 1) and the chief fraction was purified further from benzene–trichloromethane (1 : 1), yielding the *spiran* as yellow plates (50 mg), m.p. 180—181.5°, $\nu_{max.}$ 1 688, 1 595, 1 380, 1 361, 1 090, 783, and 775 cm^{-1} (Found: C, 77.4; H, 6.1%; M^+, 400.16836. $C_{26}H_{24}O_4$ requires C, 78.0; H, 6.0%; M, 400.16745).

Oxidation of this spiran (40 mg) with iron(III) chloride (200 mg) in absolute ethanol (15 ml) heated on the steam-bath for 2 h gave a dark solution that was kept for 12 h then poured into water (30 ml) and extracted with chloroform (2 × 25 ml). Isolated from the extract in the usual way, the product separated from chloroform as yellow needles, m.p. 277—278°, indistinguishable from authentic 3,3'-dimethyl-2,2'-ethylene-1,4-naphthoquinone.[14]

Ethers of 4a,9a-Dihydro-7-hydroxy-2,3,4a,5,6,8,9a-heptamethylxanthen-1,4-dione.—The hydroxy-dione [4] (5) (diduroquinone) (5 g) was methylated in the same way as the analogue (9) but for 24 h. The product separated from light petroleum giving the *methyl ether* (6) as lemon-yellow needles (5 g), m.p. 130—131.5°, $\nu_{max.}$ 1 670, 1 690sh, 1 257, and 1 210 cm^{-1} (Found: C, 73.6; H, 7.9%; M^+, 342. $C_{21}H_{26}O_4$ requires C, 73.7; H, 7.7%; M, 342).

The reaction of the hydroxy-dione with 2-iodopropane in refluxing acetone containing potassium carbonate gave the required ether but less effectively than the following method. The hydroxy-dione (2.0 g) was dissolved in absolute ethanol (13 ml) containing potassium hydroxide (0.4 g) and heated with 2-iodopropane in absolute ethanol (32 ml) for 4.5 h. The mixture was concentrated to half its bulk and added to water (250 ml), and the products were extracted into ether (3 × 50 ml) and isolated in the usual way as a yellow mass. Purification of this from light petroleum supplied the *isopropyl ether* (7) as lemon-yellow needles (1.66 g), m.p. 132°, $\nu_{max.}$ 1 688, 1 670, 1 255, 1 120, and 945 cm^{-1} (Found: C, 74.8; H, 8.1%, M^+, 370. $C_{23}H_{30}O_4$ requires C, 74.6; H, 8.1%; M, 370).

Reduction of the Xanthenedione (6) *with Zinc*.—(i) *In acetic acid*. The methoxy-xanthendione (6) (2.0 g) was reduced with zince dust in acetic acid, and tetramethylquinol removed as described for the analogue (10). After removal of tetramethylquinol, the acetic acid solution was poured into water (200 ml) and extracted with ether (3 × 80 ml). Processed in the conventional way, the extract supplied a pale yellow oil largely soluble in light petroleum; filtration and concentration supplied a product that gradually crystallised giving *2-hydroxy-5-methoxy-3,4,6-trimethylbenzyl acetate* (13) as needles (790 mg), m.p. 69—70°, $\nu_{max.}$ 3 410, 1 700, 1 290, and 1 082 cm^{-1} (Found: C, 65.7; H, 7.9%; M^+, 238. $C_{13}H_{18}O_4$ requires C, 65.5; H, 7.6; M, 238).

(ii) *In trifluoroacetic acid*. Reduction of the methoxyxanthen (6) (1.0 g) was conducted as in (i) but with tetrahydrofuran (20 ml) and trifluoroacetic acid (4 ml) as cosolvents instead of acetic acid. The reaction appeared to be complete within 5 min. The hot mixture was filtered and the residue washed with a little hot tetrahydrofuran. The combined filtrates were concentrated to half their bulk and diluted with light petroleum (15 ml) to precipitate tetramethylquinol (370 mg). After removal of this, the solution was concentrated to a small volume and mixed with water (25 ml) to precipitate the crude product (571 mg) which, after intensive drying *in vacuo* (P_2O_5), was extracted with benzene. Concentration of the benzene extract and dilution with light petroleum furnished 4-methoxy-2,3,5,6-tetramethylphenol (14) as needles, m.p. 115° (lit.,[15] 116°), $\nu_{max.}$ 3 390br, 1 258, 1 085, and 1 015 cm^{-1}.

Thermolysis of the Benzyl Acetate (13).—*In neat mesitylene*. The benzyl acetate (0.2 g) was heated in refluxing mesitylene (dried over sodium and re-distilled; 20 ml) through which oxygen-free nitrogen was blown to remove acetic acid continuously. When acetic acid could no longer be detected in the effluent (about 1 h), the solution was concentrated

TABLE 3

^1H N.m.r. spectra (τ scale)[a] of compounds derived from naphthalene (in $CDCl_3$ at 100 MHz)

	Compound				
Assignment	(10)	(24)	(23)[b]	(25)[c]	(26)
ArH[d]	1.75—1.93	1.70—1.90	1.84—2.04	1.71—1.92	1.86—2.10
ArH[d]	1.93—2.15	1.90—2.26	2.24—2.42	1.92—2.17	2.16—2.40
ArH[e]	2.45—2.80	2.26—2.76	2.44—2.68	2.51—3.01	2.40—2.70
CH_3OAr	6.22	6.20	6.16	6.23	7.03
CH_3O vinyl		6.30			
CH_AH_B	6.85[f]				
	7.51				
$ArCH_2{\cdot}CH_2Ar$				7.05	
$ArCH_2{\cdot}CH_2$ alkyl		7.16—7.50			
$ArCH_2{\cdot}CH_2$ alkyl		7.66—8.02			
$ArCH_3$	7.78	7.74	7.56	7.50	
$ArCH_3$			7.63		
Vinyl CH_3	7.98[g]	7.96			7.94[g]
Vinyl CH_3	8.02[g]				8.02[g]
$CH_3C(O{\cdot})(CO{\cdot})$	8.48				
$CH_3C(CH_2{\cdot})(CO{\cdot})$	8.71				
OH				5.43 (2 H)[i]	1.49[h]

[a] Coupling constants in Hz. All bands had the appropriate relative intensities. [b] As the acetate; τ (AcO) 7.79. [c] With 1% [$^2H_6$]dimethyl sulphoxide. [d] α-Proton; J *ca.* 8 and *ca.* 1 Hz. [e] β-Proton; overlapping multiplets. [f] J 17 Hz. [g] Broadened by homoallylic coupling. [h] Removed by contact with D_2O.

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[15] H. Eilingsfeld and C. Martius, *Annalen*, 1957, **607**, 159.

under reduced pressure to a gum, transformed by addition of light petroleum into a yellowish powder. This crystallised from light petroleum to give the trimer (20), 3′,4′,9,9a-*tetrahydro*-6′,7,9a-*trimethoxy*-1,2,4a,5,5′,6,7,7′,8,8′-*nonamethyl*-3H-*xanthen*-4(4aH)-*spiro*-2′-*chromen*-3-*one*, as light yellow needles (0.1 g), m.p. 190°, $\nu_{max.}$ 1 670, 1 410, 1 260, 1 092, 1 065, and 1 010 cm^{-1}, τ (benzene) 6.53 (3 H, s, OMe) 6.67 (6 H, s, OMe), 7.71 (3 H, s, $ArCH_3$) 7.75 (6 H, s, $ArCH_3$), 7.80 (3 H, 2, $ArCH_3$), 7.88 (3 H, s, $ArCH_3$), 7.89 (3 H, s, $ArCH_3$), 8.39 (6 H, s, vinylic Me), 8.58 (3 H, s, angular Me), 6.8—7.2 (multiplets overlapped by other bands, ring CH_2). (Found: C, 74.15; H, 8.2%; M^+, 534. $C_{33}H_{42}O_6$ requires C, 74.1; H, 7.9%; *M*, 534).

(ii) *In mesitylene containing stilbene.* The experiment in (i) was repeated except for the presence of *trans*-stilbene (2 g). A similar work-up gave a gum that was chromatographed on silica from benzene–light petroleum (1 : 1) to remove the excess of stilbene (*ca.* 1.9 g). Elution with neat benzene then gave the product, which separated from light petroleum to furnish trans-6-*methoxy*-5,7,8-*trimethyl*-2,3-*diphenylchroman* (21) as needles (20 mg), m.p. 185°; $\nu_{max.}$ 1 498, 1 410, 1 240, 1 096, 777, and 710 cm^{-1} (Found: M^+, 358.1917. $C_{25}H_{26}O_2$ requires *M*, 358.1932). Elution was completed using benzene–ether (1 : 1) and supplied the trimer (20) (82 mg).

Preparation and Thermolysis of 2-*Hydroxy*-5-*isopropoxy*-3,4,6-*trimethylbenzyl Acetate* (17).—The reduction of the isopropyl ether (7) in acetic acid occurred exactly as described for the methyl ether except that the product was much more soluble in the usual organic solvents and was therefore crystallised from light petroleum by slowly chilling the solution to about −10 °C. Thus obtained, the *isopropoxyacetate* formed needles, m.p. 70°, $\nu_{max.}$ 3 360, 1 700, 1 282, 1 082, and 970 cm^{-1} (Found: C, 67.5; H, 8.5%; M^+, 266. $C_{15}H_{22}O_4$ requires C, 67.6; H, 8.3%; *M*, 266).

Thermolysis of this acetate in a variety of solvents including xylene, mesitylene, and 2,4,6-trimethylpyridine gave tetramethyl-1,4-benzoquinone as the only isolable product.

2-*Chloromethyl*-4-*methoxy*-3,5,6-*trimethylphenol* (16).—The methoxybenzyl acetate (13) (3 g) in ether (sodium-dry; 50 ml) was added gradually to a stirred slurry of lithium aluminium hydride (500 mg) in ether (20 ml) at 0 °C. After a further 20 min the mixture was quenched with saturated aqueous sodium potassium tartrate. After the aqueous layer had been adjusted to neutrality it was discarded and the product obtained from the ethereal solution in the usual manner. The gummy solid crystallised from light petroleum giving 2-*hydroxymethyl*-4-*methoxy*-3,5,6-*trimethylphenol* (15) as leaflets (1.1 g), m.p. 123—124°; $\nu_{max.}$ 3 420, 1 408, 1 002, 825, and 715 cm^{-1} (Found: C, 67.4; H, 8.4%; M^+, 196. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%; *M*, 196).

Hydrogen chloride was bubbled through sulphuric acid and then into a solution at 0 °C of the hydroxymethylphenol (0.5 g) in ether (sodium-dry; 40 ml) containing molecular sieve and protected by a calcium chloride guard-tube. The flow was kept as rapid as convenience allowed for 40 min, then the mixture was kept at 0 °C for 15 min, and finally permitted to reach room temperature. The ether was decanted and the molecular sieve washed with ether (3 × 5 ml). The combined ether solutions were concentrated under reduced pressure, the temperature being kept below 5 °C. The product (0.48 g) which crystallised out during this process was pure enough for further synthetic work. For analysis, the product was purified by sublimation (68° and 1.0 mmHg), giving the *chloromethylphenol* as needles, m.p. 95°, $\nu_{max.}$ 3 400, 1 612, 1 280, 1 252, 1 165, 1 094, 1 003, 935, 865, 820, 778, and 721 cm^{-1} (Found: C, 61.8; H, 7.3; Cl, 16.9%; M^+, 216/214. $C_{11}H_{15}ClO_2$ requires C, 61.5; H, 7.3; Cl, 16.5%; *M*, 216/214).

5′,6-*Dimethoxy*-3′,4′,5,6′,7,8-*hexamethylchroman*-2-*spiro*-1′-*cyclohexa*-3′,5′-*dien*-2′-*one* (4).—The chloromethylphenol (16) (420 mg) in ether (250 ml) was shaken with saturated aqueous sodium hydrogen carbonate. The ether turned deep yellow at once; eventually this colour faded to lime-green and changed no further. Concentration of the ethereal layer supplied a gum that crystallised from hexane furnishing the *spirodienone* as yellow needles (280 mg), m.p. 137—138°, $\lambda_{max.}$ 228, 280sh, 286, and 325 nm (log ε 4.05, 3.56, 3.60, and 3.60), $\nu_{max.}$ 1 663, 1 649sh, 1 581, 1 255, 1 098, 1 008, and 885 cm^{-1} (Found: C, 74.1; H, 7.7%; M^+, 356. $C_{22}H_{28}O_4$ requires C, 74.1; H, 7.9%; *M*, 356).

5′,6-*Di*-*isopropoxy*-3′,4′,5,6′,7,8-*hexamethylchroman*-2-*spiro*-1′-*cyclohexa*-3′,5′-*dien*-2′-*one* (4; Me_2CHO *for* MeO).—2-Hydroxy-5-isopropoxy-3,4,6-trimethylbenzyl acetate (17) (3 g) was reduced with lithium aluminium hydride as described for the methoxy-analogue. Obtained thus, 2-*hydroxymethyl*-4-*isopropoxy*-3,5,6-*trimethylphenol* (18) separated from light petroleum as leaflets (1.0 g), m.p. 97—98°, $\nu_{max.}$ 3 500, 1 260, 1 090, and 1 000 cm^{-1} (Found: C, 69.5; H, 8.9%; M^+, 224. $C_{13}H_{20}O_3$ requires C, 69.6; H, 9.0%; *M*, 224).

Prepared from this phenol by the method described for the methoxy analogue and in similar yields, 2-*chloromethyl*-4-*isopropoxy*-3,5,6-*trimethylphenol* (19) sublimed (76° and 1.5 mmHg) giving needles, m.p. 84—85°, $\nu_{max.}$ 3 460, 1 604, 1 248, 1 110, 1 082, 952, 846, 810, 765, and 705 cm^{-1} (Found: C, 64.6; 7.7%; M^+, 244/242. $C_{13}H_{19}ClO_2$ requires C, 64.3; 7.9%; *M*, 244/242).

Treated with sodium hydrogen carbonate in the same way as the methoxy analogue, the chloromethylphenol (19) (0.5 g) supplied the *spirodienone* which crystallised from hexane as yellow needles (0.24 g), m.p. 133°, $\lambda_{max.}$ 228, 281sh, 287, and 330 nm (log ε 4.05, 3.52, 3.56, and 3.53), $\nu_{max.}$ 1 665, 1 648sh, 1 582, 1 378, 1 329, 1 248, 1 175, 1 092, and 991 cm^{-1} (Found: C, 75.3; H, 8.8%; M^+, 412.25973. $C_{26}H_{36}O_4$ requires C, 75.7; 8.8%; *M*, 412.26134).

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