

## Oxidative C-Demethylation in Phenols

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Oxidation of the complex naphthol derivative (Ia) by iron(III) chloride in ethanol gives the 1,2-naphthoquinone derivative (III) through loss of the aromatic methyl group. There is an intermediate stage which is reached quickly and appears to give a mixture of products including the stereoisomeric spirans (XIX). Though there are some differences, a general similarity is pointed out between these reactions and oxidations to quinones and spirans in the tocopherol series. No specific precursor was identified.

In the preceding paper<sup>1</sup> the proof was completed for the structure (Ia) † of the bridge trione obtained by base-catalysed addition of trimethyl-1,4-benzoquinone to the xanthen derivative<sup>2</sup> (II). In this paper we describe the unusual oxidation of the bridge trione by ethanolic iron(III) chloride which gives the naphthoquinone derivative (III) after elimination of an aromatic methyl group. In comparison with that of the acetate (Ib), the n.m.r. spectrum (Table I and Figure) of the quinone

When the new quinone is treated with weak aqueous base the solution becomes intensely purple and then orange-yellow upon acidification. Retrogressive aldol

TABLE I  
<sup>1</sup>H N.m.r. data for solutions in CDCl<sub>3</sub> (τ values)

Assignments *	Acetate (Ib)		Quinone (III)	
	Alcohol	Trichloroacetyl-carbamate	Alcohol	Trichloroacetyl-carbamate
Me <sup>a</sup>	7.51	7.56		
Me <sup>b</sup>	7.70	7.72		
Me <sup>c</sup>	8.43	8.32	8.47	8.31
Me <sup>d</sup>	7.99 †	8.08 †	8.04 †	8.00 †
Me <sup>e</sup>	8.32 †	8.32 †	8.36 †	8.31 †
Me <sup>f</sup>	8.91	8.65	8.85	8.55
Me <sup>g</sup>	8.17	8.17	8.18	8.14
Me <sup>h</sup>	8.17	8.17	8.18	8.17
CH <sub>2</sub> (ring a)	7.24 †	7.22 †	7.56 §	7.50 §
CH (ring c)	6.64 †	6.63 †	6.73 §	6.73 §
OH	6.89	6.87	7.02	6.96
NH	6.60 ¶		6.70 ¶	
ArH	1.88—2.40 (4 H) **	1.87—2.40 (4 H) **	2.17—2.60 (3 H) **	2.17—2.60 (3 H) **

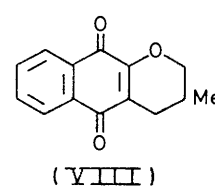
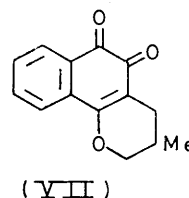
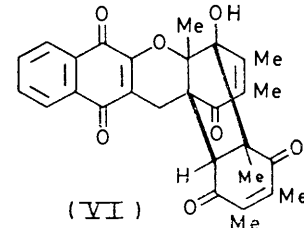
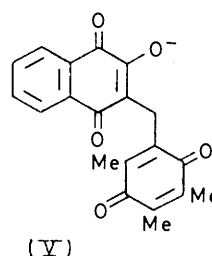
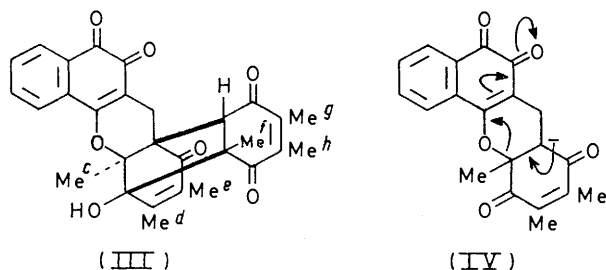
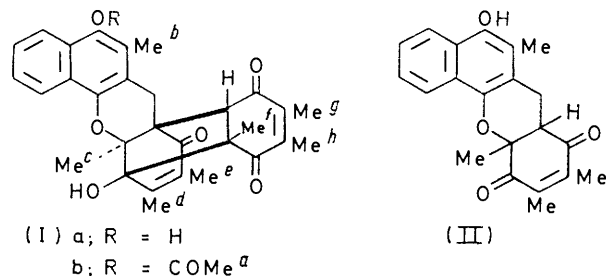
\* Designations as in ref. 2. † Slight broadening by long range coupling. ‡ d, *J* 18 Hz. § d, *J* 19 Hz. ¶ Removed by deuteration. \*\* Unanalysed multiplets. †† dd, *J* ca. 8 and 2 Hz.

shows that all the structural features of the bridge trione are intact with the exception of the hydroxy- and aromatic methyl groups, the slight differences in some chemical shifts being merely those consequent upon loss of aromaticity in one ring. The most significant of these shifts are signalled by one of the ring methylene protons (upfield) and by the angular methyl group Me<sup>f</sup> (downfield) which no longer experiences strong shielding. Esterification of the tertiary hydroxy-group in the quinone by trichloroacetyl isocyanate confirms that no other hydroxy-group is present and produces a number of shifts closely parallel to those in the bridge trione so that the oxidation cannot have induced any change in stereochemistry.

† This and other diagrams represent racemates.

<sup>1</sup> F. M. Dean, L. E. Houghton, G. Mitchell, B. Parvizi, and C. Thebtaranonth, preceding paper.

<sup>2</sup> F. M. Dean, K. B. Hindley, and L. E. Houghton, *J. Chem. Soc. (C)*, 1971, 1171.



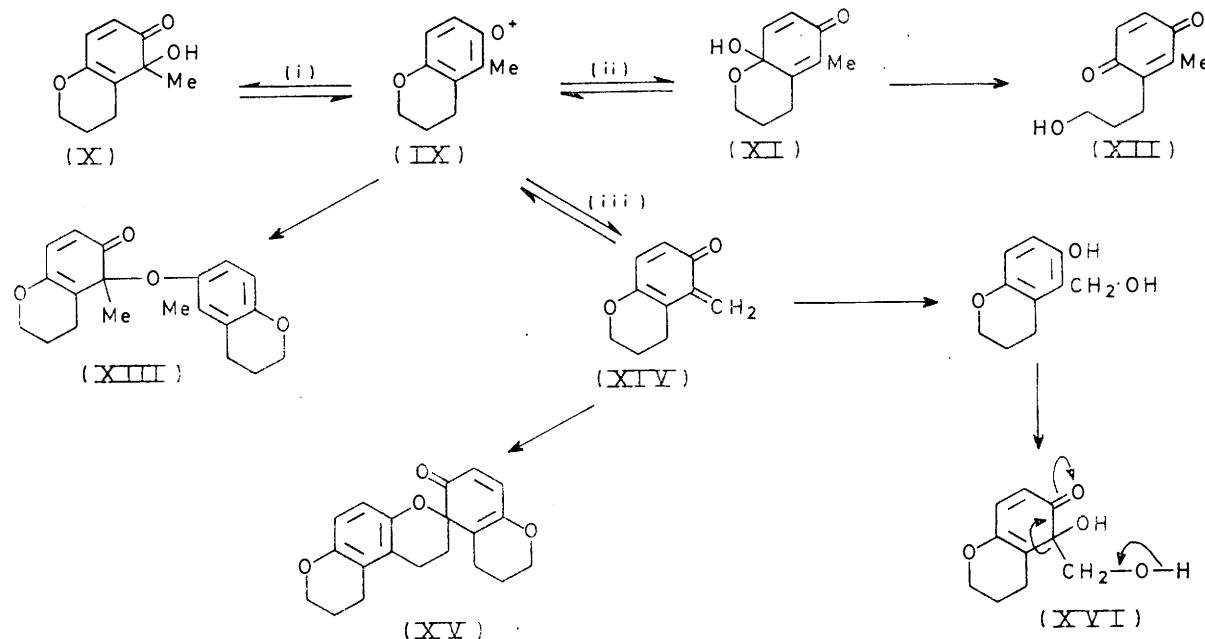
and Michael reactions would detach the bridge system from the quinone (III) as from the parent bridge trione<sup>2</sup> giving trimethyl-1,4-benzoquinone along with the carbanion (IV) in which the electronic movements indicated would expose the oxyanion (V) responsible for the purple colour. The colour changes resemble those

shown by lawsone (2-hydroxy-1,4-naphthoquinone) in alkali but no precise study could be made because the spectra of the alkaline solutions varied with time and we were unable to isolate any product other than trimethyl-1,4-benzoquinone from them.

None of the evidence discussed so far adequately established the 1,2-quinonoid (III) as opposed to the 1,4-quinonoid structure (VI), which could have been reached in several ways including acid-catalysed rearrangement of the 1,2-quinone as in the conversion of

them giving overlapping bands above  $\tau$  2 and one of them giving a doublet of doublets at substantially lower field ( $\tau$  1.9); hence one proton differs from the other three because of deshielding by an adjacent carbonyl group, and structure (III) follows.

The loss of an aromatic methyl group in so mild an oxidation is rare except in the tocopherol series.<sup>5</sup> In both cases derivatives of quinol are attacked, whereas their acetates are stable, and we agree with Martius and Eilingsfeld<sup>6</sup> that iron(III) salts should be able to oxidise



(VII) into (VIII) studied by Ettlinger.<sup>3</sup> Though the i.r. spectrum of (III) is remarkably similar to that of 1,2-naphthoquinone in the carbonyl region, the correspondence must be largely fortuitous because of the additional carbonyl groups present; on the other hand, the electronic spectrum clearly favours the 1,2-quinone formulation since, apart from the bands near 250 nm due to the enone and enedione groupings, it is very close to that of (VII) especially with respect to the definitive band at longest wavelengths (Table 2).

The mass spectrum adds support to the 1,2-quinone formulation: the expected molecular ion at  $m/e$  466 is accompanied by another at  $m/e$  468. At 70 eV the intensity ratio is 92 : 100, and even at 14 eV it is 100 : 46. Though the acquisition of hydrogen atoms in the mass spectrometer is found to some extent in all quinones, only in 1,2-quinones is it so marked.<sup>4</sup> Finally, the n.m.r. spectrum favours the 1,2-quinone formulation. The aromatic protons resonate as multiplets, three of

them to the oxygen cation state, *i.e.* to phenoxylum ions, a state for which we and others have now adduced

TABLE 2  
Comparison of the electronic spectra\* of the quinones (III), (VII), and (VIII)

(IV)		(VII)		(VIII)	
$\lambda/nm$	$\log \epsilon$	$\lambda/nm$	$\log \epsilon$	$\lambda/nm$	$\log \epsilon$
246	4.57	256	4.42	250	4.37
252	4.58				
259	4.46				
274sh	4.26	280sh	3.72	281	4.13
335	3.27	330	3.20	333	3.45
422	3.17	427	3.24	375sh	3.07

\* *ca.*  $10^{-3}M$ -Solutions in ethanol.

much evidence.<sup>7</sup> The Scheme shows that such a cation (IX) may react with water as in step (i) giving a dienone alcohol (X) or as in step (ii) giving a dienone acetal (XI) which offers opportunity for ring opening to a quinone alcohol (XII). Reaction between the cation

<sup>3</sup> E. Alder and R. Magnusson, *Acta Chem. Scand.*, 1959, **13**, 505; K. Dimroth, W. Umbach, and H. Thomas, *Chem. Ber.*, 1967, **100**, 132; F. R. Hewgill and B. S. Middleton, *J. Chem. Soc. (C)*, 1967, 2316; M. S. Chauhan, F. M. Dean, K. B. Hindley, and M. L. Robinson, *Chem. Comm.*, 1971, 1141; J. W. A. Findlay, P. Gupta, and J. R. Lewis, *Chem. Comm.*, 1969, 207; W. A. Waters, *J. Chem. Soc. (B)*, 1971, 2026.

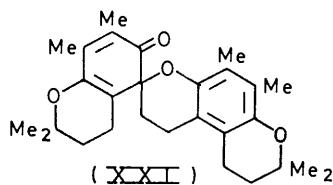
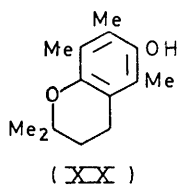
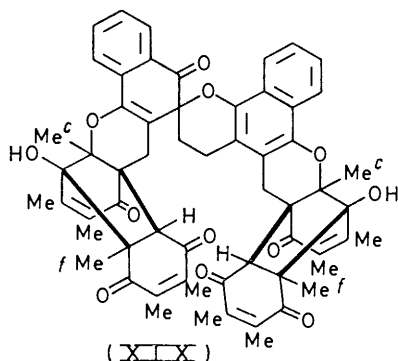
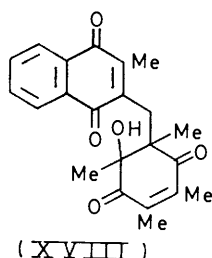
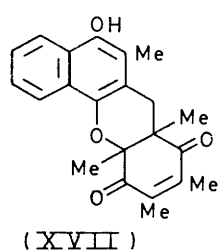
<sup>3</sup> M. G. Ettlinger, *J. Amer. Chem. Soc.*, 1950, **72**, 3090.

<sup>4</sup> R. W. A. Oliver and R. M. Rashman, *J. Chem. Soc. (B)*, 1971, 341.

<sup>5</sup> L. I. Smith, W. B. Irwin, and H. E. Ungnade, *J. Amer. Chem. Soc.*, 1939, **66**, 2424; V. L. Frampton, W. A. Skinner, and P. S. Bailey, *ibid.*, 1954, **76**, 282.

<sup>6</sup> C. Martius and H. Eilingsfeld, *Annalen*, 1957, **607**, 159.

and unchanged phenol would give related products, e.g. the dimeric ether (XIII). Alternatively, water or



some other base may remove a proton from the cation (IX) [step (iii)] leaving a quinone methide (XIV). By itself this would dimerise giving a spiran (XV), but it should also be capable of undergoing the further reactions shown leading to a diol (XVI), which undergoes elimination of the methyl carbon atom as formaldehyde as shown to give finally a 1,2-quinone. The oxidative formation of quinone methides is a well established feature of tocopherol chemistry<sup>8</sup> and has recently been generalised by Bolon.<sup>9</sup> The steps in which formaldehyde is eliminated are directly related to those found in the demethylation of methylquinones by amines after the initial quinone methide stage has been attained by tautomerisation.<sup>10</sup>

As a rule, oxidation by iron salts follows step (ii) (Scheme) and gives a quinone alcohol of type (XII), and the monoalkyl ethers of simple quinol derivatives show the same pattern of reaction.<sup>6,11</sup> Even relatively complicated quinol derivatives behave thus,<sup>12,13</sup> as when iron(III) chloride oxidises the xanthen derivative (XVII)

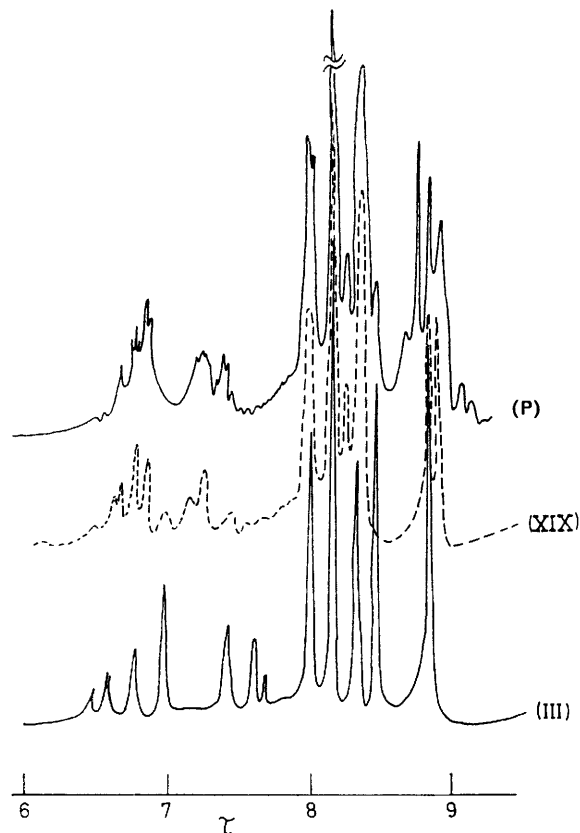
<sup>8</sup> F. W. Knapp and A. L. Tappel, *J. Amer. Oil. Chemists' Soc.*, 1961, **38**, 151; W. A. Skinner and R. M. Parkhurst, *ibid.*, 1964, **29**, 3601; J. L. G. Nilsson, J.-O. Brånstad, and H. Sievertsson, *Acta Pharm. Suecica*, 1968, **5**, 509; A. Merijan, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, 1963, **28**, 2148.

<sup>9</sup> D. A. Bolon, *J. Org. Chem.*, 1970, **35**, 715, 3666.

<sup>10</sup> W. M. Horspool, P. I. Smith, and J. M. Tedder, *J.C.S. Perkin I*, 1972, 1024.

to the quinone alcohol<sup>13</sup> (XVIII). The change to step (iii) and demethylation is therefore dictated by the bridge system in (Ia) and from models it appears that a steric effect could be important. The methyl groups Me<sup>e</sup> and Me<sup>f</sup> project over and under the heterocyclic ether link so that this area is not readily accessible to attack, and the approach of water molecules would be hampered in step (ii) (Scheme) but not in step (i) or (iii).

Attempts to detect formaldehyde or equivalent products were not successful, but a moderated oxidation shows that the first stage of the reaction is complete in a few minutes and gives a yellowish material (P) which is gradually broken down into the quinone during about 2 h though some of it survives much longer. The yellowish material is difficult to chromatograph or crystallise, but elemental analysis and the mass spectrum



N.m.r. spectrum (solvent  $\text{CDCl}_3$ ) of the quinone (III), the spiran(s) (XIX), and the amorphous oxidation product (P)

suggest the formulation  $\text{C}_{30}\text{H}_{28-30}\text{O}_6$  which hardly differs from that of the starting phenol. The n.m.r. spectrum (Figure) discloses no major change. We must therefore

<sup>11</sup> W. John, E. Dietzel, and W. Emte, *J. Physiol. Chem.*, 1939, **257**, 173; M. Tishler and N. L. Wendler, *J. Amer. Chem. Soc.*, 1941, **63**, 1532; V. W. Goodlett, *Analyt. Chem.*, 1965, **37**, 431; I. R. Trehan and C. Monder, *Tetrahedron Letters*, 1968, 67; W. Durckheimer and L. A. Cohen, *Biochem. Biophys. Res. Comm.*, 1962, **9**, 262.

<sup>12</sup> L. I. Smith, R. W. H. Tess, and G. E. Ulliyot, *J. Amer. Chem. Soc.*, 1944, **66**, 1320; K. Chandrasenan and R. H. Thompson, *J. Chem. Soc. (C)*, 1966, 1320.

<sup>13</sup> F. M. Dean and L. E. Houghton, *J. Chem. Soc. (C)*, 1968, 2060.

assume that product (P) is a mixture of dimers which dissociate readily in the mass spectrometer; vapour phase osmometry indicated a molecular weight of 1 080 which supports the dimeric character of the bulk of the material but indicates the presence of trimers or higher polymers as well.

A small amount of a crystalline substance was obtainable from the amorphous mass and had the molecular formula  $C_{60}H_{56}O_{12}$  although the molecular ion at  $m/e$  968 was very weak and almost too fugitive for study. This substance is therefore at an oxidation level appropriate to a quinone methide of type (XIV). The dimerisation of *ortho*-quinone methides is well known to yield spirans<sup>14</sup> and in some cases trimers are also observed.<sup>8,9</sup> Consequently the crystalline substance can be allocated structure (XIX) and a new i.r. band at  $1\ 698\text{ cm}^{-1}$  can be assigned to the benzoyl carbonyl group of the spiran system. Related spirans have been observed to undergo cycloreversion<sup>15</sup> to quinone methides when heated, and in recent parallel studies<sup>16</sup> we have noted extensive dissociations at temperatures as low as  $80\text{ }^{\circ}\text{C}$ , thus fully explaining the behaviour of the substance in the mass spectrometer. By itself the cycloreversion would yield a 'parent' ion at  $m/e$  484, not 486 as observed, but since an *ortho*-quinonoid formulation is again involved the uptake of 2H can be expected. In structure (XIX) the two bridge systems are not identical; on one side there is a naphthalene ring as in the starting phenol but on the other this has been transformed into an *ortho*-quinonoid dienone system. The n.m.r. spectrum (Figure) reflects these features surprisingly well; it shows the absence of an aromatic methyl group  $\text{Me}^b$  and permits correlation of all the other methyl bands with those in the starting bridge trione or the quinone (III) finally obtained. In most areas the resonances of the two moieties are similar so that the bands appear broad rather than as doublets, but the angular methyl group  $\text{Me}^f$ , which is the one best placed to detect changes in aromaticity, gives a clear 'doublet' near  $\tau\ 9$  with branches of equal intensity, one as in (Ib) and the other as in (III). But the methylenic and other protons gave too complex a spectrum for individual allocations though the general integration was satisfactory. However, because the two bridge moieties of the spiran are different, structure (XIX) embraces four racemates and since these would all have very similar properties we are uncertain whether the crystalline substance is a single compound even though it is chromatographically homogeneous.

In the tocopherol series the course of the oxidation is

<sup>14</sup> A. B. Turner, *Quart. Rev.*, 1964, **18**, 347; H.-U. Wagner and R. Gommper, in 'The Chemistry of Quinonoid Compounds,' ed. S. Patai, Wiley, London, 1974, p. 1145.

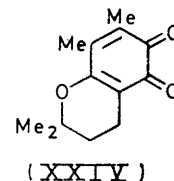
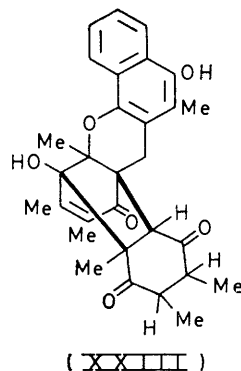
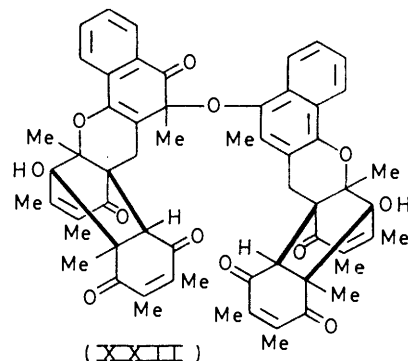
<sup>15</sup> M. S. Chauhan, F. M. Dean, D. A. Matkin, and M. L. Robinson, *J.C.S. Perkin I*, 1973, 120; J. L. G. Nilsson and H. Sievertsson, *Acta Pharm. Suecica*, 1968, **5**, 517.

<sup>16</sup> D. A. Matkin, Ph.D. Thesis, Liverpool, 1975.

<sup>17</sup> J. L. G. Nilsson, G. D. Daves, and K. Folkers, *Acta Chem. Scand.*, 1968, **22**, 207.

<sup>18</sup> W. A. Skinner and R. M. Parkhurst, *J. Org. Chem.*, 1966, **31**, 1248.

strongly dependent upon the oxidant and the conditions. Iron salts have not been found to yield either spirans or dimeric ethers, so the two series are not precisely analogous. Tocopherol spirans are easily obtained, however, by oxidations utilising quinones,<sup>17</sup> benzoyl peroxide,<sup>18</sup> or alkaline hexacyanoferrate,<sup>19</sup> and it is known that quinone methides are intermediates.<sup>8</sup> Such oxidations are commonly believed to involve radicals at some stage, but as the reagents seemed insufficiently specific for use with the bridge trione (Ia) we examined the use of the 6-phenyl-2,4-di-*t*-butylphenoxy radical<sup>20</sup> and found that it rapidly oxidises the tocopherol analogue (XX) to the spiran (XXI). It also oxidises the bridge trione to a yellowish amorphous



product (P) indistinguishable from that obtained by use of iron salts. The reaction is smooth enough to allow a semiquantitative estimate of the oxidation level of the mixed product; removal of 2H per molecule must result in products at the quinone methide or spiran level, and of 1H in products such as the alcohol (X) or a dimeric ether<sup>17,21</sup> such as (XXII). In practice the radical was consumed to the extent of 1.7H per molecule of bridge trione, suggesting that the product is *ca.* 70% spiran. The presence of dimeric ethers or related

<sup>19</sup> P. Schudel, H. Mayer, J. Metzger, R. Rüegg, and O. Isler, *Helv. Chim. Acta*, 1963, **46**, 636.

<sup>20</sup> E. Müller, A. Schick, R. Mayer, and K. Scheffler, *Chem. Ber.*, 1960, **93**, 2649.

<sup>21</sup> R. Pummerer and I. Viet, *Chem. Ber.*, 1953, **86**, 412; A. Rieker, N. Zeller, K. Schurr, and E. Müller, *Annalen*, 1966, **697**, 1; H.-D. Becker, *J. Org. Chem.*, 1969, **34**, 1203; W. J. Mijs, O. E. van Lohuizen, J. Bussink, and L. Wibaut, *Tetrahedron*, 1967, **23**, 2253.

species was then checked by reduction of the oxidation product with zinc in acetic acid, which can be expected to break the ether link and also reduce the enedione groupings, thus giving (XXIII). Though this compound<sup>2</sup> was obtained in only about 2% yield, the fact does confirm the presence of such species.

As oxidation by the iron salt to the quinone proceeds, the amorphous yellow material slowly diminishes, but after 3 h some still survives, and it now has n.m.r. and i.r. spectra that conform to those of the spirans (XIX). This suggests that the spiran is not a precursor of the quinone but is merely suffering general degradation, a view supported by the iron(III) oxidation of the model spiran (XXI) which gives no *ortho*-quinone (XXIV) under conditions in which the phenol (XX) gives it readily. It is therefore likely that the quinone is generated mainly *via* the dimeric ether fraction that has escaped characterisation. We hope to find a simpler case of oxidative demethylation that will permit more precise studies.

#### EXPERIMENTAL

(7aR\*,7bR\*,11aR\*,12R\*,12aS\*)-7b,11a,12,12a-Tetrahydro-12-hydroxy-9,10,11a,12a,14,15-hexamethyl-7H-12,7a-propenoindeno[2,1-b]naphtho[2,1-e]pyran-5,6,8,11,16-pentaone (III).—A hot solution of the bridge trione<sup>2</sup> (Ia) (0.43 g) in ethanol (20 ml) was mixed with iron(III) chloride (1.4 g) in ethanol (20 ml) and left on a steam-bath for 2 h. The cooled mixture was diluted with water (400 ml) and extracted with ether (3 × 20 ml). The combined extracts were dried (MgSO<sub>4</sub>) and concentrated *in vacuo* until a solid was obtained which could be purified by recrystallisation from benzene giving the pentaone as fine orange needles (0.14 g), m.p. 330°,  $\nu_{\max}$  3 520 (OH), 1 695, 1 665, 1 648, 1 638, and 1 600 cm<sup>-1</sup> (under the same conditions 1,2-naphthoquinone had  $\nu_{\max}$  1 694, 1 658, 1 614, and 1 592 cm<sup>-1</sup>) (Found: C, 71.7; H, 5.3. C<sub>29</sub>H<sub>26</sub>O<sub>7</sub> requires C, 71.6; H, 5.4%). A solution (*ca.* 10<sup>-4</sup>M) of this compound in ethanol had  $\lambda_{\max}$  422 nm (log  $\epsilon$  3.17); addition of one drop of aqueous 0.2M-sodium hydroxide changed this to  $\lambda_{\max}$  *ca.* 477 nm (log  $\epsilon$  3.32) (measured after 1 min; varies with time). Acidification of the alkaline solution with acetic acid, then left a solution with  $\lambda_{\max}$  325, 284inf, 272inf, and 254 nm. In comparative experiments 2-hydroxy-1,4-naphthoquinone in alkaline solution had  $\lambda_{\max}$  464 nm, shifted to 336 nm by acidification; thus a shift of 128 nm in this long wavelength band is compared with one of 152 nm for base-treated bridge pentaone. Methylenequinones related to (V) are themselves susceptible to base.<sup>22</sup>

The quinone (50 mg) in ether-benzene (1 : 1; 20 ml) was shaken with aqueous 0.2M-sodium hydroxide (10 ml) at 0 °C for 5 min. The purple aqueous layer was discarded. The organic layer was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated *in vacuo*. The residue was chromatographed on silica from light petroleum-benzene and gave one major yellow band from which elution extracted trimethyl-1,4-benzoquinone (8 mg) identical (spectra; mixed m.p.) with authentic material.

*Oxidation of the Bridge Trione (Ia) to the Spiran (XIX).*—

<sup>22</sup> F. M. Dean and L. E. Houghton, *Tetrahedron Letters*, 1969, 3578.

<sup>23</sup> L. I. Smith, H. E. Ungnade, H. H. Hoehn, and S. Wawzonek, *J. Org. Chem.*, 1939, 4, 311.

(i) The foregoing oxidation was repeated with monitoring by t.l.c.; after about 6 min the substrate (Ia) had almost entirely disappeared although the quinone (III) was present only in traces. The product was precipitated by water and dried *in vacuo* at 18 °C but attempts to chromatograph it failed because of extensive streaking. By dissolving the product in benzene and chilling the solution we obtained a better sample and several repetitions gave material which behaved coherently when chromatographed on silica. This material, product (P), formed a yellowish powder (0.39 g) with no distinctive m.p. (Found: C, 74.2; H, 6.2. Calc. for C<sub>60</sub>H<sub>56</sub>O<sub>12</sub>: C, 74.2; H, 6.0). Vapour phase osmometry in benzene gave  $M$  1 070 ± 36 (Calc. for C<sub>60</sub>H<sub>56</sub>O<sub>12</sub>:  $M$ , 970). Crystallisation from benzene gave a substance believed to be the spiran (XIX) as pale yellow needles, m.p. 265° (decomp.),  $\nu_{\max}$  3 510 (OH), 1 698 (benzoyl C:O), 1 661 (other C:O), 1 621, and 1 598 cm<sup>-1</sup> (Found: C, 74.1; H, 6.2. Calc. for C<sub>60</sub>H<sub>56</sub>O<sub>12</sub>: C, 74.4; H, 5.8%).

(ii) A solution of the 6-phenyl-2,4-di-*t*-butylphenoxy radical in wet benzene was prepared according to Müller *et al.*<sup>20</sup> and freed from water droplets but not otherwise dried. It was added slowly to the bridge trione (Ia) (0.68 g) in benzene (200 ml) and reacted almost instantly. Addition was continued until a faint green colour persisted. After 16 h the solution was concentrated under reduced pressure and light petroleum added until precipitation was complete. The amorphous yellowish solid (0.68 g) was collected and chromatographed on silica, and the fraction eluted with benzene-trichloromethane (4 : 1) retained to give a yellowish material indistinguishable from that obtained in (i). It partly crystallised from ether giving the spirans (XIX) as yellow needles, m.p. 263–265°, chromatographically and spectroscopically identical with a sample prepared as in (i). Use of standardised radical solutions under nitrogen showed that the green colour persisted after the uptake of radical equivalent to 1.7H per molecule of bridge trione.

*Zinc-Acetic Acid Reductions.*—The amorphous yellow solid (0.6 g) from (ii) above was treated in acetic acid (20 ml) with zinc dust (0.8 g) and kept at about 80 °C for 5 h. The filtered solution was diluted with benzene and washed with water several times, then its contents were chromatographed on silica from benzene and benzene-trichloromethane to give, in one fraction, the reduced bridge trione (XXIII), which crystallised from benzene as faintly yellow prisms (18 mg), m.p. 234–237°, chromatographically and spectroscopically identical with an authentic sample.<sup>2</sup> Other fractions gave substances that appear to be reduced forms of the spirans (XIX). They were not closely investigated.

*Oxidations of 2,2,5,7,8-Pentamethylchroman-6-ol.*—(i) The chroman<sup>23</sup> (200 mg) was treated in benzene (10 ml) with a solution of the 6-phenyl-2,4-di-*t*-butylphenoxy radical<sup>20</sup> in benzene until the green colour persisted. Chromatography of the product on alumina (20 g) with benzene-pentane (1 : 1) gave as the main fraction the spiran (XXI) (145 mg) identical with an authentic specimen.<sup>24</sup>

(ii) The chroman (0.5 g) in methanol (20 ml) was heated with iron(III) chloride (2.5 g) at 50 °C for 2 h. The cooled solution was diluted with water and the products were collected into ether, washed with water, and recovered as a red oil which, after purification on a column of silica, gave

<sup>24</sup> W. A. Skinner and P. Alaupovic, *J. Org. Chem.*, 1963, 28, 2854.

the quinone (XXIV) (19 mg), identical with an authentic specimen.<sup>5</sup> In the same conditions the spiran (XXI) failed to give any trace of the quinone (XXIV) detectable by chromatography.

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