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Periodate Oxidation of Phenols

IX. Oxidation of *o*-(ω-Hydroxyalkyl)phenols *,[1]

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The oxidation of salicyl alcohol with sodium metaperiodate in aqueous solution was found to result in the formation of spiroepoxy-2,4-cyclohexadienone *5*, which, however, could not be isolated, since it dimerised rapidly by Diels-Alder reaction to give compound *7*. Analogous dimers (*12b* – *14b*) were obtained from the 3,5-dimethyl, the 3-hydroxymethyl-5-methyl, and the 3-methoxy derivatives of salicyl alcohol, one of several possible dimers only being observed in each case. Periodate oxidation of two homologs of salicyl alcohol was also examined. 2-(2-Hydroxyphenyl)ethanol gave the same dimeric spirooxirane (*7*) as had been obtained from salicyl alcohol, one mol of formaldehyde per mol of starting material being liberated. The next homolog, 3-(2-hydroxyphenyl)propanol, reacted in the normal way, to give the dimeric spirooxolane *27*.

Oxidation of certain 2-methylphenols, *viz.* 2,4- and 2,6-dimethylphenol, as well as mesitol, with aqueous sodium periodate was previously shown to result in the formation of *o*-quinols (6-hydroxy-6-methyl-2,4-cyclohexadienones), which spontaneously dimerised by Diels-Alder reaction.[2,3] *o*-Quinols obtained from 2-methylphenols carrying a substituent in the 3-position, however, were found to be stable as monomers,[4,5] dimerisation being sterically hindered.[6]

Periodate oxidation of salicyl alcohol. In analogy to the behaviour of 2-methylphenols unsubstituted in the 3-position, salicyl alcohol (*1*) on treatment with periodate could be expected to give an *o*-quinol (*2*), which probably would undergo glycol cleavage to yield *o*-benzoquinone. Instead, a high yield of the dimer (*7*) of the spiroepoxycyclohexadienone *5* and a small amount of salicylaldehyde were obtained.

The assignment of structure *7* to the major reaction product is based on the following evidence.

The presence of a conjugated and an isolated keto group is indicated by IR bands at 1688 and 1734 cm^{-1}, the unusually high frequency of the latter

* Dedicated to Professor Eugen Müller, Tübingen, on occasion of his 65th birthday.

band probably being due to ring strain. Bands at 1620 and 1652 cm^{-1} are due to the ethylenic double bonds. The UV absorption spectrum of the compound (Fig. 1) shows the K-band of the α,β-enone system (λ_{max} at 232 nm, calc. 227 nm; $\varepsilon = 8820$), as well as a band of similar intensity at 202 nm ($\varepsilon = 9640$). This short-wavelength band, previously encountered in the absorption spectra of dimeric *o*-quinols,[3] is caused by transannular charge transfer between the ethylene bridge and the 2-keto group in the photoexcited state [7a] ("photodesmotic" band [7b]). This homoconjugated enone system also causes the enhancement of the $n \rightarrow \pi^*$ band (λ_{max} 310 nm),[7,8] the intensity of which ($\varepsilon = 160$) is higher than that expected for the sum of the ε values of an α,β-unsaturated and an isolated keto group.

The IR spectrum of compound *7* shows a peak at 3040 cm^{-1} which is assigned to the methylene groups of the two oxirane rings. In the 60 Mc NMR spectrum of the substance, obtained with DMSO-d_6 as solvent, the protons of each of the oxirane CH_2 groups show geminal coupling giving rise to AB patterns. One of the pairs of doublets is centered around δ 2.87, the other one around δ 3.02 ppm, the geminal coupling constants being 6.5 and 6.0 cps, respectively.

Treatment of *7* in dioxane with aqueous hydrogen bromide [9] provided the bis(bromohydrin) *8*, which crystallised with $\frac{1}{2}$ mol of dioxane, and was obtained in a solvent-free state by recrystallisation from benzene. It still shows the UV (Fig. 1) and IR characteristics of the two ketonic systems, whereas the C–H stretching vibration of the oxirane rings at 3040 cm^{-1} is lacking. When the bis(bromohydrin) *8* was treated with methanolic potassium hydroxide, the bis(oxirane) *7* was regenerated.

The presence of tertiary rather than primary hydroxyl groups in the bis(bromohydrin) was confirmed by the fact that the compound did not react with chromium trioxide in glacial acetic acid.[10] Attempts to esterify the two tertiary hydroxyl groups of *8* with $AcOAc/HClO_4$, using the method described by Fritz and Schenk,[11] resulted in the formation of a monoacetate (*8a*, UV absorption, see Fig. 1), only the hydroxyl group present in the unbridged ring being acetylated. The position of the acetoxyl group is indicated by the fact that the IR peak of the conjugated keto group of the monoacetate (1706 cm^{-1}) is shifted by 23 cm^{-1} towards higher wavenumbers as compared with that of the (dioxane-free) starting material *8* (1683 cm^{-1}), whereas the peak of the non-conjugated keto group (1728 cm^{-1}) is unchanged.

Similar IR-shifts have previously been observed on acetylation of dimeric *o*-quinols; the stretching absorptions of the conjugated as well as of the isolated carbonyl groups of these compounds were shifted by about 20 cm^{-1} towards higher wavenumbers when the adjacent tertiary hydroxyl groups were acetylated (Ref. 3, pp. 1595–1596). The previously described pair of compounds [1] *10*, with ν_{CO} 1658, and *10a*, with ν_{CO} 1680 cm^{-1} (ester-CO 1745 cm^{-1}, all values in KBr), represents another example related to the pair *8* and *8a*. Furthermore, a similar behaviour has been reported for α-hydroxyketone side-chains and the corresponding α-acetoxyketone side-chains in steroids.[12]

If acetic acid rather than dioxane was used as solvent in the hydrogen bromide treatment of *7*, cleavage of the oxirane rings was accompanied by the loss of one mol of H_2O and aromatisation of the cyclohexenone ring, compound *11* being formed. The same compound was obtained when the

HBr – HOAc mixture was allowed to act upon the bis(bromohydrin) *8*. The UV absorption of *11* (Fig. 2) was very similar to that of the analogous "anhydrodimers" of *o*-quinols,[3] the long-wavelength shoulder at 315 nm (log ε 2.96, in 80 % ethanol) indicating an enhanced $n \rightarrow \pi^*$ transition, which is due to transannular interaction between the π-electrons of the benzene ring and the keto group in β-position to this ring.[8] A strong red-shift of the maxima taking place on addition of alkali (Fig. 2) confirmed the presence of a phenolic group. Treatment with $AcOAc/HClO_4$ [11] converted *11* into the diacetate *11a* (UV spectrum, Fig. 2).

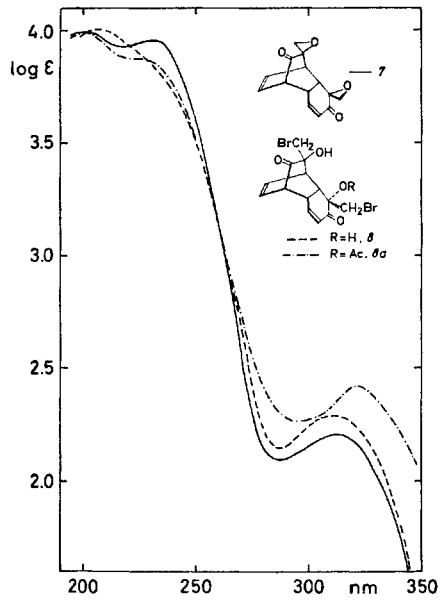


Fig. 1. Ultraviolet spectra. Solvent, 99.5 % ethanol.

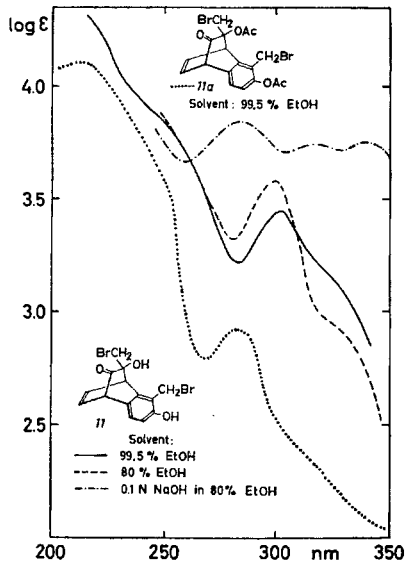
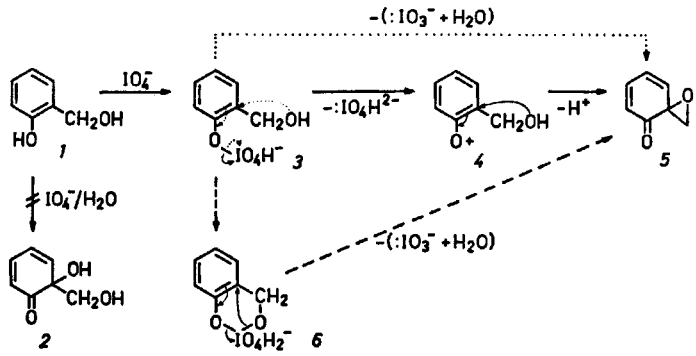
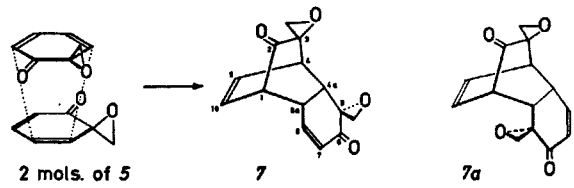


Fig. 2. Ultraviolet spectra. Solvents, see figure.

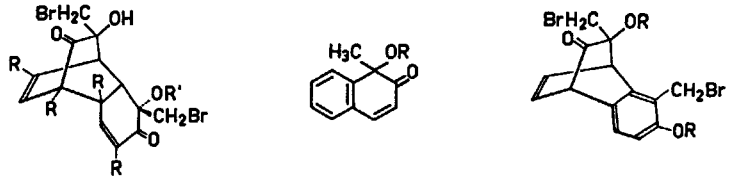
The evidence presented above proves the product obtained on periodate oxidation of salicyl alcohol to be a Diels-Alder dimer of the spiroepoxycyclohexadienone *5*. Three possible pathways for the formation of the monomeric intermediate *5* are given in Scheme 1. The common initial step is assumed to be the nucleophilic addition of the phenolic hydroxyl group of *1* to the periodate (*cf.* also Ref. 1) to give the periodic ester *3*. Two-electron transfer would lead to the phenoxonium ion *4*, which by intramolecular nucleophilic attack of the alcohol oxygen atom on the ring carbon atom 2 would give the epoxide *5* (Scheme 1, full line arrows). The conversion *3*→*5* can also be thought to proceed as a single-step concerted reaction (dotted line arrows) or as a two-step reaction with the cyclic periodic ester *6* as an intermediate (dashed line arrows). The essential feature of the over-all reaction is the fact that the alcohol oxygen of the molecule is acting as a nucleophile, although water



Scheme 1.



Scheme 2.



8 R=R'=H
8a R=H ; R'=$COCH_3$
9 R=CH_3 ; R'=H

10 R=H
10a R=$COCH_3$

11 R=H
11a R=$COCH_3$

is present as solvent. Nucleophilic attack by water would result in the formation of the *o*-quinol type compound *2*; however, neither this compound nor conceivable conversion products thereof were obtained from the reaction mixture, the yield of dimer *7* being about 70 %.

Compound *7* was the only dimeric reaction product detected; this implies that the Diels-Adler dimerisation of the 2,4-cyclohexadienone *5* is specific or at least highly selective with regard to structural as well as stereochemical orientation.

As indicated by the presence of an α,β-enone grouping in *7*, the γ,δ-double bond of the dienophilic component is involved in the cycloaddition reaction. The same behaviour has been observed in all Diels-Alder dimerisations of 2,4-cyclohexadienones reported previously.[6]

It can be assumed that these dimerisations follow the *endo* addition rule,[13] which recently has been explained on the basis of symmetry-controlled secondary orbital interactions.[14] Experimental evidence, however, has been provided so far only in the case of the dimer of 2,6,6-trimethyl-2,4-cyclohexadienone, which has been assigned the *endo* configuration on the basis of its dipole moment.[15]

Structure *7* is the result of the *endo* addition of two *S*-enantiomers of monomer 5, oriented as shown in Scheme 2, whereas two *R*-enantiomers similarly will yield the optical antipode of *7*. An additional racemate of the dimer would arise if in the "orientation complex" (transition state) the CH_2 groups rather than the oxygen atoms (*cf.* Scheme 2) of the oxirane rings were facing each other. Furthermore, similar dimerisations involving one *S*- and one *R*-enantiomer of *5* would also permit two racemates of the dimer. In these 4 stereoisomeric dimer racemates (group A), both oxirane groups are on the same side of the molecule (*cf.* formula *7*). In a second group of 4 stereoisomeric racemates (group B), the oxirane groups would be on opposite sides of the molecule; one of the enantiomers of this group is represented by formula *7a*.

According to a rule put forward by Horner and Dürckheimer,[16] the formation of dimers belonging to group A, such as compound *7*, should be more probable, because the arrangement of the keto groups causes the transition state to have a dipole moment, which is lower than that of the transition state for the formation of the structural isomers belonging to group B, such as *7a*. In fact, a structural orientation of the type occurring in *7* was established, by chemical degradation, for the dimer of 6-hydroxy-6-methyl-2,4-cyclohexadienone acetate.[17] The configuration at carbon atoms 3 and 5 of the latter dimer, however, remained undetermined.

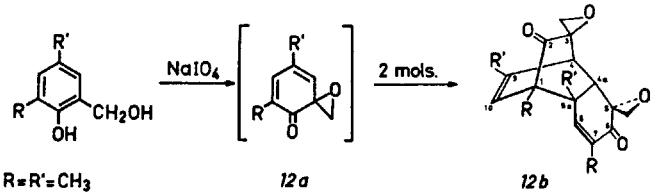
Of the various possible stereoisomers belonging to group A, compound *7* and its optical antipode can be assumed to be favoured for steric reasons. In the "orientation complex" leading to *7* (see Scheme 2), with the oxirane oxygen atoms directed inward, there will be less steric repulsion than in the remaining possible arrangements, in which one or both CH_2 groups of the oxirane rings are pointing towards the middle of the complexes. For the dimer of 6-fluoro-2,6-dimethyl-2,4-cyclohexadienone, Kende and MacGregor,[8] on the basis of chemical and spectral evidence, as well as similar consideration of the steric requirements involved, had favoured a structure analogous to *7* and its antipode.

Finally, proof for the correctness of structure *7* was obtained by X-ray crystallographic analysis of the bis(bromohydrin) *8* containing 1/2 mol of dioxane.[18] The results of this analysis established structure *8* for the bis(bromohydrin) and, consequently, also structure *7* for the dimeric periodate oxidation product of salicyl alcohol. The dimerisation of the intermediate spirooxirane *5* thus must proceed *via* the *endo* transition state indicated in Scheme 2, and its mirror image, respectively. This seems to represent the first example of a completely elucidated dimerisation of a 2,4-cyclohexadienone containing an asymmetric sp^3 carbon atom.

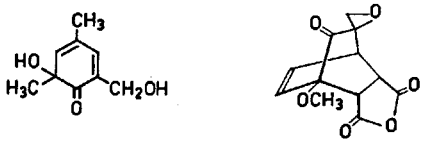
Periodate oxidation of ring-substituted salicyl alcohols. In analogy to the results obtained with salicyl alcohol (*1*), periodate oxidation of three ring-substituted salicyl alcohols, *viz.* 2-hydroxymethyl-4,6-dimethylphenol (*12*),

2,6-bis(hydroxymethyl)-4-methylphenol (*13*), and *o*-vanillyl alcohol (*14*), gave the corresponding dimeric spiroepoxycyclohexadienones (*12b*, *13b*, *14b*). (For preliminary observations regarding the periodate oxidation of *o*-vanillyl alcohol, see Ref. 19.) In none of these cases, the monomeric oxidation product (*12a*, *13a*, *14a*) was observed, dimerisation taking place rapidly. Elemental analyses and molecular weight data were in accordance with the postulated structures (*12b* – *14b*). These were further supported by the spectral properties of the dimers. Thus, the locations of the $\pi \rightarrow \pi^*$ transitions of the α,β-enone systems (see Fig. 3) are close to the calculated ones; this is also true for the UV maximum of dimer *14b*, which appears at 272 nm, this exceptional long-wavelength location being caused by the α-methoxyl substituent (calculated value [20] 262 nm). The UV spectra further show the "photodesmotic" band, as well as the intensified $n \rightarrow \pi^*$ carbonyl absorption due to the homoconjugated ketone system (maxima at 204 and 315 nm, and at 206 and 318 nm for *12b* and *13b*, respectively, and shoulders at about 215 and 320 nm in the case of *14b*). The presence of two oxirane rings in *12b* was confirmed by the finding that treatment with hydrobromic acid in dioxane gave the bis(bromohydrin) *9* (UV absorption, see Fig. 3), from which methanolic potassium hydroxide regenerated the starting material.

In the 60 Mc NMR spectrum of dimer *12b* (in acetone-d_6), the axial proton at position 4a appears as a doublet at δ 2.24 ppm, whereas the signal for the equatorial proton at position 4 (δ 2.53) is a triplet due to vicinal coupling with H – 4a and allylic coupling with H – 10, the coupling constants $J_{4,4a}$ and $J_{4,10}$ being very similar ($\sim$2.3 cps). These data confirm the structural



12 R=R'=CH_3 *12a* *12b*
13 R=CH_2OH ; R'=CH_3 *13a* *13b*
14 R=CH_3O ; R'=H *14a* *14b*



15 *16*

orientation given in formula *12b*, which is the same as that of the unsubstituted dimer *7* (see p. 2059). If the dimer were the orientation isomer corresponding to formula *7a*, carbon atom 4a would carry a methyl group, whereas a hydrogen atom would be located at position 8a and give rise to a singlet.

Similar NMR analysis of dimer *13b* indicated its structural orientation to be the same as that found for dimers *7* and *12b*, this orientation being in accord with the rule of Horner and Dürckheimer [16] mentioned above (p. 2059).

On the basis of these experimental results, the analogous diene-dienophile orientation was assumed for the dimer obtained on periodate oxidation of *o*-vanillyl alcohol (*14b*). Furthermore, it has been assumed that the steric configuration at carbon atoms 3 and 5 in dimers *12b* – *14b* is the same as in dimer *7*. Studies are in progress to examine whether the specific structural orientation found in the Diels-Alder dimers *7*, *12b*, and *13b*, as well as the specific stereochemistry demonstrated so far only for dimer *7* are of general validity for dimers of 2,4-cyclohexadienones carrying an asymmetric sp^3 carbon atom.

The dimers *12b*, *13b*, and *14b* were obtained in yields of 75, 70, and 52 %, when the corresponding *o*-hydroxybenzyl alcohols *12*, *13*, and *14* were treated with sodium periodate in aqueous solutions. The fair yields of these dimers indicate that the formation of the spiroepoxycyclohexadienones *12a*, *13a*, and *14a* successfully competes with other possible reactions. Such reactions could be mainly the formation of the *o*-quinol *15* from phenol *12*, and the oxidative demethylation of phenol *14* to give an *o*-quinone and methanol; reactions of these types were previously found to proceed rapidly on periodate oxidation of *o*-methyl- and *o*-methoxyl-substituted phenols, respectively.[1–3,19] Neither *o*-quinol *15* nor its dimer were found to be by-products in the periodate oxidation of phenol *12*. However, methanol was rapidly liberated in a yield of 20 % on oxidation of phenol *14*; no attempts were made to demonstrate the presence of the expected 3-hydroxymethyl-1,2-benzoquinone in the brownish-red reaction mixture, from which the main product, *i.e.* dimer *14b*, began to crystallise after a few minutes.

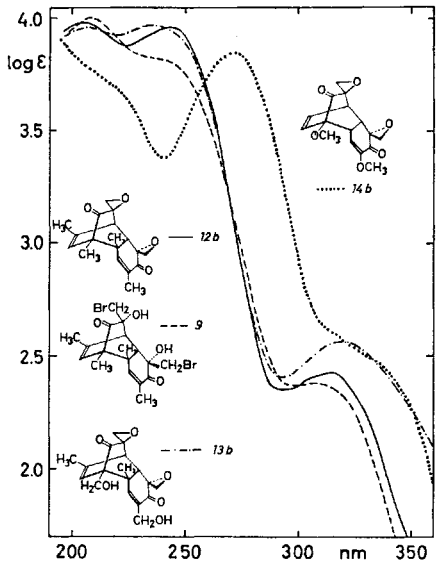


Fig. 3. Ultraviolet spectra. Solvent, 99.5 % ethanol.

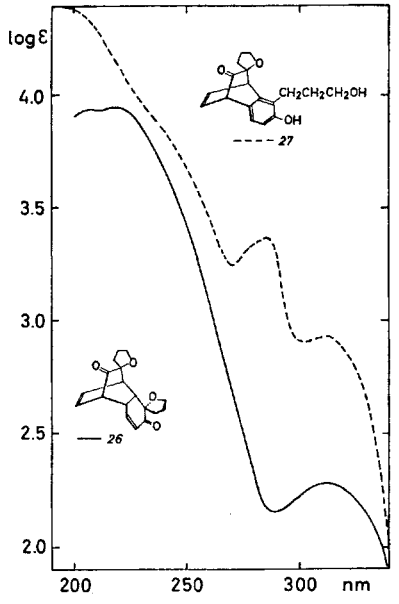
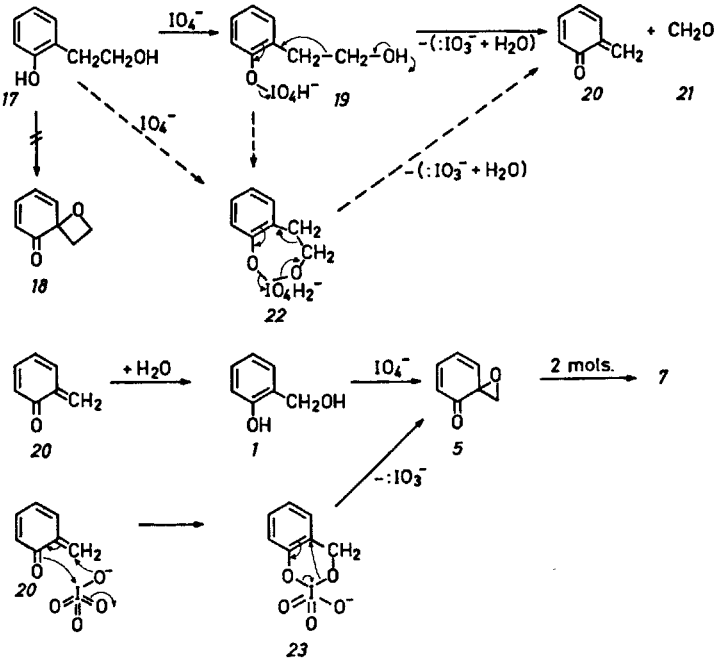


Fig. 4. Ultraviolet spectra. Solvent, 99.5 % ethanol.

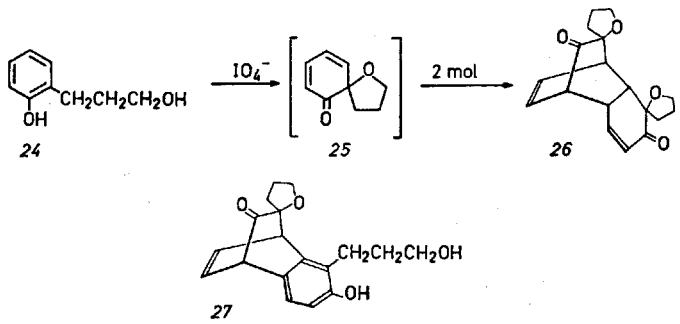
For two of the dimers reported in this paper, namely *7* and *14b*, *retro*-Diels-Alder reaction has been examined. Upon heating above its melting point, dimer *7* gave salicylaldehyde, albeit in low yield, whereas *o*-vanillin was obtained from *14b*. Apparently, the primarily formed monomeric spiroepoxycyclohexadienones *5* and *14a*, respectively, rearrange to the corresponding aromatic aldehydes at the reaction temperature (about 200°); such thermal isomerisation of unsymmetrically substituted epoxides to aldehydes is well-known.[21] When the thermolysis of dimer *14b* was carried out in the presence of maleic anhydride, the monomeric epoxide *14a* was trapped, to give the Diels-Alder adduct *16*. Similar trapping of 2,4-cyclohexadienones by maleic anhydride has been reported earlier.[22]

Periodate oxidation of two homologs of salicyl alcohol. It was of interest to investigate the behaviour on periodate oxidation of homologs of salicyl alcohol, in which the CH_2OH substituent was replaced by $(CH_2)_nOH$. The compounds with $n=2$ (*17*) and $n=3$ (*24*) were investigated. If the oxidation of these compounds proceeds in analogy to that of salicyl alcohol (Scheme 1), the formation of spirooxetane *18* and spirooxolane *25*, respectively, or the corresponding dimers could be expected.

The periodate oxidation of 2-(2-hydroxyphenyl)ethanol (*17*) neither gave the oxetane *18* nor its dimer, but, surprisingly, resulted in the formation of 1 mol of formaldehyde and bis(oxirane) *7*, which had been obtained from salicyl alcohol. Obviously, carbon-carbon cleavage of the ω-hydroxyethyl side-chain of *17* had taken place.



Scheme 3.



Possible pathways for this reaction are presented in Scheme 3. The periodic aryl ester *19* (*cf.* the corresponding ester *3* in Scheme 1) is assumed to decompose by two-electron transfer with concomitant cleavage of the side-chain, to give *o*-quinone methide (*20*) and formaldehyde (*21*). (This reaction may also be thought to proceed in two steps, *viz.* formation of the phenoxonium ion, corresponding to ion *4* in Scheme 1, followed by its decomposition into *20* and *21*.) An alternative route would be formation of the seven-membered cyclic periodic ester *22* (*cf.* the similar ester *6* in Scheme 1) and its decomposition to products *20* and *21* (Scheme 3, dashed arrows).

o-Quinone methide (*20*) has been shown to be formed on pyrolysis of *o*-(methoxymethyl)phenol and found to trimerise spontaneously already at rather low temperature.[23] In the slightly acidic aqueous medium used in our experiments, *o*-quinone methide can be expected to add water to give salicyl alcohol (*1*); the latter, by excess periodate present, will rapidly be converted to the epoxide *5*, which dimerises to product *7*. Alternatively, the intermediate *o*-quinone methide may add a molecule of periodate instead of water; the resulting cyclic ester *23* (or its hydrate *6*, *cf.* Scheme 1) would decompose to iodate and the epoxide *5*.

The unexpected oxidative degradation of phenol *17* to *o*-quinone methide (*20*) and formaldehyde (*21*) may be regarded as the cleavage of a vinylogous 1,2-glycol (*17*) and thus seems to represent an extension of the classical cleavage reactions brought about by periodate. The assumption of the seven-membered cyclic ester *22* as an intermediate then would be in harmony with the experimentally supported formation of 5-membered cyclic periodic esters as intermediates in the cleavage of ordinary 1,2-glycols.[24]

In contrast to phenol *17*, its next homolog, 3-(2-hydroxyphenyl)propanol (*24*), reacted with aqueous periodate in the expected manner, the dimer *26* of the hypothetical intermediate *25* being obtained in good yield (UV absorption, see Fig. 4). Treatment of *26* with hydrogen bromide in dioxane solution resulted in proton-catalysed opening of the spirooxolane ring located at the unbridged cyclohexenone ring, followed by aromatisation of the latter ring, phenol *27* being formed. Its UV spectrum (Fig. 4) was very similar to that of compound *11*, as well as to the UV spectra of compounds of the same structural type derived from dimeric *o*-quinols.[3]

EXPERIMENTAL

Ultraviolet spectra were recorded using a Cary Model 14 spectrophotometer; infrared and NMR spectra were obtained using Beckman 9A and Varian A-60 instruments, respectively. Chemical shifts are given in δ (ppm) units, TMS being used as internal standard. Melting points are uncorrected.

1,3,4,4a,5,8a-Hexahydro-1,4-ethenonaphthalene-3,5-bis(spirooxirane)-2,6-dione (7). When a 0.02 M aqueous solution of saligenin (*2*) was mixed with an equal volume of 0.14 M aqueous sodium metaperiodate, 1 mol of the oxidant per mol of *1* was consumed during about 2 min, and there was only inappreciable further periodate consumption. For isolation of compound *7*, a solution of $NaIO_4$ (47.0 g, 0.22 mol) in 1 l of water was added to a stirred solution of saligenin (24.83 g, 0.20 mol) in 1.5 l of water. After about 10 min, colourless crystals began to deposit. The mixture was kept in the dark for 24 h at 4°. The crystalline solid formed was collected, washed with water and dried in a vacuum desiccator over P_2O_5 (yield 74%). Colourless prisms from chloroform or acetone. When heated rapidly in a bath preheated to 160°, the substance melted at 194–195°. (Found: C 68.98; H 5.00; O 26.04. Calc. for $C_{14}H_{12}O_4$: C 68.84; H 4.95; O 26.21.)

Extraction of the aqueous filtrate with ether gave a small amount of an oily product, which was converted into a 2,4-dinitrophenylhydrazone (0.3 g), identical by m.p. and mixed m.p. with the 2,4-dinitrophenylhydrazone of *salicylaldehyde*.

***Estimation of oxirane groups in* 7. The method of Ross [25] was used.** A solution of 0.5 mmol (0.1215 g) of compound *7* in 2 ml of acetone was mixed with 40 ml of a 0.2 M solution of sodium thiosulfate in acetone - water (1 : 1), and a few drops of phenolphthalein solution were added. The mixture was heated to 30° and the pH kept approximately constant (faint pink colour) by continuous addition of 0.2026 N acetic acid. After about 20 min, the mixture was refluxed for some minutes and again titrated with acetic acid. In two experiments, the total consumption of acetic acid was 4.95 and 4.90 ml; calc. for two oxirane groups per molecule: 4.91 ml.

Thermal decomposition of compound 7. The dimer (112 mg) was heated under vacuum (12 mm) for 8 min at 205° (bath temp.) in a small distillation tube. The nearly colourless distillate (36 mg) contained salicylaldehyde, as demonstrated by preparation if its 2,4-dinitrophenylhydrazone; spectrophotometric examination of an alcoholic solution of the distillate, using the absorption maximum at 325 nm, indicated a yield of 15 mg of the aldehyde, constituting 14 % based on dimer *7*. By thin layer chromatography, as well as by isolation after chromatography on a silica gel column (elution with benzene - ethyl acetate 4 : 1), the remainder of the distillate was shown to consist mainly of saligenin, apparently formed by some oxidation-reduction process.

1,3,4,4a,5,8a-Hexahydro-3,5-bis(bromomethyl)-3,5-dihydroxy-1,4-ethenonaphthalene-2,6-dione (8). Aqueous hydrobromic acid (12.3 g of a 66 % solution, 100 mmol HBr) was added dropwise to a solution of dimer *7* (2.44 g, 10 mmol) in dioxane (300 ml). After 24 h at room temperature, the solution was concentrated *in vacuo* to one third of its volume, when colourless crystals began to deposit. Recrystallisation of the crude product, m.p. 155–160°, from acetone gave plates of m.p. 160–167° (decomp.), which contained 0.5 mol of dioxane per mol of *8* (yield 72 %); the dioxane was retained on repeated recrystallisation from acetone, and was not released on 4 h drying *in vacuo* at 40°. It was readily detected by gas chromatographic examination of a solution of the substance in glacial acetic acid. (Found: C 42.78; H 4.19; Br 35.66. Calc. for $C_{14}H_{14}O_4Br_2.0.5\ C_4H_8O_2$: C 42.68; H 4.03; Br 35.51.) IR (KBr): ν_{max} (cm^{-1}) 1622 (C=C), 1700 (conj. CO), 1727 (CO), 3340 (broad, OH), 3470 (sharp, OH), as well as bands due to dioxane at 870, 1110, and 1255 cm^{-1}. X-Ray crystallographic data, see Ref. 18.

When the dioxane-containing compound in the crude state or after recrystallisation from acetone (see above) was recrystallised from benzene, a benzene-containing product was obtained, from which the benzene could be removed by drying over paraffin at 50° *in vacuo* for 4 days. M.p. 172–173°. (Found: C 41.41; H 3.56; Br 39.49. Calc. for $C_{14}H_{14}O_4Br_2$: C 41.42; H 3.48; Br 39.36.) IR (KBr): ν_{max} (cm^{-1}) 1622, 1645 (C=C), 1683 (conj. CO), 1731 (CO), 3410 (broad, OH), 3458 (sharp, OH).

The solvent-free compound was readily soluble in acetone; after addition of a small amount of dioxane, crystals of the compound containing 0.5 mol of dioxane deposited, identical by IR with the dioxane complex described above.

Regeneration of bis(oxirane) 7 *from bis(bromohydrin)* 8. A solution of bis(bromohydrin) *8* (0.5 mmol) in methanol was mixed with 0.1 M methanolic potassium hydroxide (12 ml). After 10 min, water was added and the mixture extracted with chloroform. The extract gave a nearly quantitative yield of crude dimer *7*, identified after recrystallisation from acetone by m.p., mixed m.p. and IR spectrum.

Monoacetate 8a. The dioxane complex of bis(bromohydrin) *8* (450 mg) was dissolved in 10 ml of the EtOAc-AcOAc – $HClO_4$ reagent, described by Fritz and Schenk.[11] After 10 min, the mixture was extracted with water and then with aqueous bicarbonate; the ethyl acetate phase was dried over $CaSO_4$ and evaporated *in vacuo*. The semi-solid residue after one recrystallisation from acetone-hexane gave a 53 % yield of *8a*, m.p. 135 – 139°; further recrystallisation from the same solvent mixture raised the m.p. to 140 – 141°. (Found: C 43.00; H 3.73; Br 35.83; CH_3CO 8.87. Calc. for $C_{16}H_{16}O_5Br_2$: C 42.87; H 3.60; Br 35.66; CH_3CO 9.60.) IR (KBr): ν_{max} 3510 cm^{-1} (sharp, OH); see also p. 2056. NMR (DMSO-d_6): δ 2.18 (singlet, 3H, CH_3CO), 3.46 (singlet, 2H, CH_2Br, partially overlapped by signals for 3 CH), 4.14 and 4.26 (1 H each, doublets, $J = 11$ cps, AB system of second CH_2Br), 5.8 – 6.8 (4 olefinic H).

The monoacetate *8a* was converted into dimer *7* by treatment with KOH – CH_3OH in the same way as described above for the bis(bromohydrin) *8*.

3,4-Dihydro-3,5-bis(bromomethyl)-3,6-dihydroxy-1,4-ethenonaphthalen-2(1H)-one (11). Aqueous hydrobromic acid (12.3 g of 66 % solution, 100 mmol HBr) was added slowly to a solution of dimer *7* (2.44 g, 10 mmol) in the necessary amount of glacial acetic acid. After 24 h, the solution was concentrated *in vacuo* to one third of its volume, and the crystals which deposited were collected and recrystallised from acetone-hexane (yield 52 %). The compound darkens at about 170° and decomposes without melting. (Found: C 43.43; H 3.16; Br 41.39. Calc. for $C_{14}H_{12}O_3Br_2$: C 43.33; H 3.12; Br 41.19.) IR (KBr): ν_{max} (cm^{-1}) 1497, 1597, 1605 (arom. ring), 1722 (CO), 3390 (broad, OH), 3508 (sharp, OH).

Compound *11* was also formed, when a few drops of 66 % aqueous hydrobromic acid were added to a solution of bis(bromohydrin) *8* (406 mg, 1 mmol) in glacial acetic acid. After two days, the solution, when concentrated *in vacuo*, provided compound *11*, identified by TLC and IR spectrum with the material described in the preceding section.

Diacetate 11a was obtained by dissolving phenol *11* (388 mg, 1 mmol) in 15 ml of the EtOAc – AcOAc – $HClO_4$ reagent[11] and working up the mixture after 10 min. After recrystallisation from 96 % ethanol plates of m.p. 175 – 175.5° (yield 68 %). (Found: C 45.43; H 3.47; Br 33.67; CH_3CO 16.30. Calc. for $C_{18}H_{16}O_5Br_2$: C 45.85; H 3.42; Br 33.85; CH_3CO 18.2.) IR (KBr): ν_{max} (cm^{-1}) 1470, 1594, 1606 (arom. ring), 1729 (CO), 1749 (aliph. ester), 1767 (aryl ester).

1,3,4,4a,5,8a-Hexahydro-1,7,8a,9-tetramethyl-1,4-ethenonaphthalene-3,5-bis(spirooxirane)-2,6-dione (12b). A 0.14 M aqueous solution of $NaIO_4$ (410 ml, 55 mmol) was added to a solution of 3,5-dimethylsalicyl alcohol (*12*, 7.6 g, 50 mmol) in 1.1 l of water. After about 1 h, colourless crystals began to deposit. The product collected after 24 h at 4° in the dark (yield 76 %, m.p. 137 – 138°) was recrystallised from ethanol or acetone, or purified by sublimation at 30 μHg and 115° (bath temp.). Prisms, m.p. 138.5 – 139°. (Found: C 71.97; H 6.66; O 21.25. Calc. for $C_{18}H_{20}O_4$: C 71.98; H 6.71; O 21.31.) IR (KBr): ν_{max} (cm^{-1}) 1700 (conj. CO), 1737 (CO), 3032 (oxirane-CH_2). Near infrared (EtOH): λ_{max} (μ) 1.68, 2.20 (oxirane).[29]

NMR (acetone-d_6): δ 1.28 (singlet, 6 H, CH_3-1 and CH_3-8a), 1.77 (doublet, 3 H, CH_3-7, $J_{CH_3-7,H-8} = 1.4$ cps), 1.82 (doublet, 3 H, CH_3-9, $J_{CH_3-9,H-10} = 1.65$ cps), 2.24 (broadened doublet, 1 H, H – 4a, $J_{H-4a,H-4} = 2.3$ cps), 2.53 (triplet, 1 H, H – 4, $J_{H-4,H-4a} = J_{H-4,H-10} = 2.3$ cps), 2.74 and 2.94 (doublets, 1 H each, $J = 6.6$ cps, oxirane-CH_2 at C – 3 or C – 5; the doublet due to the proton at δ 2.94 is further split into doublets, $J \sim 0.3$ cps, indicating long range coupling with H – 4 or H – 4a; *cf.* Ref. 27), 3.07 and 3.09 (doublets, 1 H each, $J = 6.3$ cps, oxirane – CH_2 at C – 3 or C – 5), 5.38 (broadened quintet, 1 H, H – 10, $J_{H-10,CH_3-9} = 1.65$, $J_{H-10,H-4} = 2.3$ cps), 6.44 (broad singlet, 1 H, H – 8). The chemical shifts of the oxirane protons show considerable solvent dependence (*cf.* also Ref. 28). Thus, in $CDCl_3$, the high field CH_2 protons appear as a singlet (δ 2.83), whereas the low field CH_2 protons exhibit an AB pattern (δ 2.97 and 3.18, $J = 6.3$ cps).

1,3,4,4a,5,8a-Hexahydro-3,5-bis(bromomethyl)-3,5-dihydroxy-1,7,8a-9-tetramethyl-1,4-ethenonaphthalene-2,6-dione (9). Aqueous hydrobromic acid (0.7 ml of a 66 % solution, 12 mmol) was added to a solution of dimer *12b* (1.50 g, 5 mmol) in dioxane (170 ml).

After 24 h, the mixture was brought to dryness *in vacuo*; the residual oil crystallised upon addition of 96 % ethanol. Recrystallisation from the same solvent gave prisms, m.p. 176 – 177.5° (yield 76 %). (Found: C 46.72; H 4.93; Br 34.55. Calc. for $C_{13}H_{22}O_4Br_2$: C 46.79; H 4.80; Br 34.56.) IR (KBr): ν_{max} (cm^{-1}) 1645, 1652 (C=C), 1689 (conj. CO), 1712 (CO), 3405 (broad, OH), 3450 (sharp, OH).

Treatment of bis(bromohydrin) *9* with a 2.4-fold excess of 0.1 M methanolic KOH for 10 min regenerated the bis(oxirane) *12b* (yield 90 %), identified by m.p., mixed m.p., and IR spectrum.

1,3,4,4a,5,8a-Hexahydro-1,7-bis(hydroxymethyl)-8a,9-dimethyl-1,4-ethenonaphthalene-3,5-bis(spirooxirane)-2,6-dione (13b).* To a cooled solution (4°) of 2,6-bis(hydroxymethyl)-*p*-cresol (*13*)[29] (1.68 g, 10 mmol) in water (600 ml), a similarly cooled aqueous solution of 0.14 M $NaIO_4$ (215 ml, 30 mmol) was added with stirring. After 40 min at 4°, excess of $NaIO_4$ was reduced by addition of ethylene glycol (5 g) and the solution extracted with twelve 200 ml portions of ethyl acetate. The extract was dried over anhydrous Na_2SO_4 and evaporated under vacuum to dryness. The crystalline residue (yield 70 %, m.p. 152 – 154°) on recrystallisation from ethyl acetate gave colourless prisms, m.p. 155 – 156° (yield 64 %). (Found: C 64.91; H 6.09. Calc. for $C_{18}H_{20}O_6$: C 65.04; H 6.07.) IR (KBr): ν_{max} (cm^{-1}) 1674 (conj. CO), 1733 (CO), 3070 (oxirane – CH_2), 3430 (broad, OH) NMR (DMSO – d_6): δ 1.26 (singlet, 3 H, CH_3 – 8a), 1.78 (doublet, 3 H, J = 1.2 cps, CH_3 – 9), 2.10 (doublet, 1 H, H – 4a), 2.69 and 2.98 (doublets, 1 H each, AB-system with J = 6.5 cps, oxirane – CH_2 at C – 3 or C – 5), 2.94 and 3.14 (doublets, 1 H each, AB-system with J = 6.0 cps, oxirane – CH_2 at C – 3 or C – 5), 3.55 – 4.15 (overlapping signals for 4 H, CH_2OH – 1 and CH_2OH – 7), 4.80 (broad, 2 H, 2 OH), 5.69 (quintet, 1 H, H – 10), 6.60 (1 H, H – 8). The signal for H – 4 is hidden by the signal for incompletely deuterated DMSO. It appears at δ 2.58 (triplet) in the spectrum of a solution in CD_3OD. In the latter solvent, only one of the oxirane-CH_2 groups gives an AB-pattern (δ 2.79 and 2.92, J = 6.5 cps), whereas the second one gives rise to a singlet at δ 3.06 (*cf.* also compound *12b*).

1,3,4,4a,5,8a-Hexahydro-1,7-dimethoxy-1,4-ethenonaphthalene-3,5-bis(spirooxirane)-2,6-dione (14b). A 0.06 M aqueous solution of $NaIO_4$ (100 ml) was added at 4° to an equal volume of a 0.06 M solution of *o*-vanillyl alcohol in water : ethanol (4 : 1, v/v). After 24 h at 4°, the crystalline precipitate formed was collected and washed with small amounts of cold ethanol (yield 52.2 %), and recrystallised by addition of hexane to a solution of the product in a mixture of chloroform and abs. ethanol. M.p. 169 – 169.5°. (Found: C 63.09; H 5.51; OCH_3 20.36. Mol.wt. cryoscopically in dioxane, 270. Calc. for $C_{16}H_{16}O_6$: C 63.16; H 5.50; OCH_3 20.40. Mol.wt. 304.31.) IR (KBr): ν_{max} 1640 (strong, C=C – OCH_3), 1700 (conj. CO), 1740 (CO), 3065 (oxirane-CH_2). NMR ($CDCl_3$): δ 2.72 – 3.28 (6 H, two AB-systems for oxirane-CH_2-groups, J = 6.0 and 6.5 cps, partially overlapped by signals for 2 CH); 3.66 and 3.68 (singlets, 3 H each, 2 OCH_3, partially overlapping multiplet for 1 CH); 5.74 – 6.66 (3 olefinic H).

Periodate oxidation of *o*-vanillyl alcohol in aqueous solution rather than in water containing 10 % ethanol (see above) gave slightly decreased yields of dimer *14b* (46.8 % and 49.1 %, when the initial concentrations of the reactants in the reaction mixture were 0.03 and 0.04 M, respectively). *Methanol* formed as a by-product was determined ** by gas chromatography.[31] A Porapak-Q column was used; trifluoroethanol was added to the reaction mixture as internal standard. The formation of methanol (0.20 mol per mol of *o*-vanillyl alcohol) was complete after a few minutes. No methanol was detected, when a solution of dimer *14b* in pure dioxane was injected into the gas chromatograph.

Estimation of oxirane groups in 14b. (*a*) *With sodium thiosulfate*[25] (*cf.* p. 2064). In two runs (at 40 and 50°, respectively), 0.50 mmol of compound *14b*, which dissolved gradually during the reaction, consumed 0.450 and 0.482 mmol $Na_2S_2O_3$; the reaction time required was about 175 min at 40°. Only one of the two epoxide groups has thus reacted with thiosulfate.

(*b*) *With hydrogen chloride in dioxane.*[30] Dioxane was purified by refluxing over NaOH and, subsequently, over sodium. A sample of compound *14b* (0.5 – 1.0 mmol) was added to a mixture of conc. aqueous hydrochloric acid and dioxane, being about 0.2 M with respect to HCl. The substance dissolved within a few minutes, giving a colourless solution. Titration with 0.1 M methanolic sodium hydroxide of samples of the reaction mixture

* Experiment performed by civiling. K. Holmberg.

** Experiments performed by fil.kand. L. Hemrå.

withdrawn at intervals indicated that HCl-consumption was complete after about 30 h. In three runs, 2.00, 1.99, and 2.10 mol of HCl per mol of compound *14b* were consumed, indicating the presence of 2 oxirane groups.

(*c*) *With hydrogen bromide in dioxane.* The reaction was complete after only 20 min, 2 mol of HBr per mol of *14b* being consumed.

Thermal decomposition of dimer 14b. The compound (608 mg) was heated for some minutes at 170–180° (bath temp.) in a small distillation apparatus, which had been flushed with nitrogen and evacuated to 10 mmHg. The light-yellow oily distillate (230 mg) partially crystallised on cooling in a mixture of dry ice and methanol. Needles (91 mg), m.p. 44.5° after recrystallisation from ethanol-water, identical with *o*-vanillin by IR spectrum.

Trapping of cyclohexadienone 14a *by maleic anhydride.* A mixture of dimer *14b* (456 mg, 1.5 mmol) and maleic anhydride (294 mg, 3.0 mmol) was rapidly heated under N_2 to 165°, a brown-yellow melt being obtained. During a period of 5 min, the temperature was gradually raised to 175°, when the oil solidified. After 5 min, the reaction mixture was cooled to room temperature, chloroform was added, and the crystalline solid was filtered off and washed with chloroform. The crude adduct *16* (m.p. 199–200°, 309 mg, yield 41 %) on recrystallisation from ethyl acetate gave needles, m.p. 210–211°. (Found: C 57.41; H 4.09; OCH_3 12.52. Mol.wt. (Rast) 265. Calc. for $C_{12}H_{10}O_6$: C 57.60; H 4.03; OCH_3 12.40. Mol.wt. 250.21.) IR (KBr): ν_{max} 1610 (C=C), 1708 (ketonic CO), 1780 and 1860 (anhydride-CO groups), 3080 (oxirane-CH_2). NMR (acetone-d_6): δ 3.20 (singlet, 2 H, oxirane-CH_2), 3.72 (singlet, 3 H, OCH_3), 3.80–4.42 (signals for 3 CH), 6.26–6.88 (signals for 2 olefinic H).

2-(2-Hydroxyphenyl)ethanol (17). A solution of 2-coumaranone [32] (9.3 g, 70 mmol) in abs. ether (300 ml) was added during a period of 50 min to a solution of $LiAlH_4$ (4.2 g, 110 mmol) in the same solvent (300 ml), nitrogen being passed through the reaction mixture. The mixture was refluxed for 3 h, excess $LiAlH_4$ was decomposed with wet ether, and the precipitate dissolved by addition of dilute sulfuric acid. The ethereal layer was washed with water and aqueous bicarbonate and gave, after drying over anhydrous calcium sulfate and evaporation, a viscous oil which was dried *in vacuo* over P_2O_5. Yield 92.5 %; $n_D = 1.5560$ (lit.[33]: $n_D^{18} = 1.5575$).

Periodate oxidation of phenol alcohol 17. A 0.14 M solution of $NaIO_4$ in 5 % aqueous acetic acid (1 l) was added to a stirred solution of 2-(2-hydroxyphenyl)ethanol (2.76 g, 20 mmol) in the same solvent (1 l). The mixture was kept in the dark for 24 h and then thoroughly extracted with methylene chloride. The extract was dried over $CaSO_4$ and evaporated, leaving a brownish solid, which was recrystallised from acetone and shown to be identical with dimer *7* by elemental analysis as well as by IR and NMR spectra.

In a separate experiment, a sample of the final reaction mixture (100 ml) was mixed with 20 % aqueous lead acetate, until no precipitate was formed on further addition of the latter solution. The precipitate consisting of lead iodate and lead periodate was centrifuged off and washed with 5 % acetic acid and water. The combined solutions were neutralised with sodium bicarbonate, and distilled in an atmosphere of nitrogen, until the volume of the remaining solution was about 15 ml. Water (20 ml) was then added, and 20 ml of the solution distilled off, and this procedure was repeated twice. The distillate was collected in a cooled receiver, charged with a mixture of a saturated aqueous solution of dimedone (80 ml) and NaOAc/HOAc buffer of pH 4.6 (220 ml, bromophenol blue as indicator).[34] The mixture was kept in a refrigerator for 24 h, and gave 271.5 mg (92.5 %) of the formaldehyde-bis-dimedone compound, m.p. 187–189°, undepressed on admixture of authentic material, m.p. 189°.

3-(2-Hydroxyphenyl)propanol (24)[35] was obtained by reduction of 3,4-dihydrocoumarin with lithium aluminum hydride, according to the procedure described above for the preparation of 2-(2-hydroxyphenyl)ethanol from 2-coumaranone.

1,3,4,4a,5,8a-Hexahydro-1,4-ethenonaphthalene-3,5-bis(2′-spirooxolane)-2,6-dione (26). 3-(2-Hydroxyphenyl)propanol (*24*) was treated with $NaIO_4$ and the reaction mixture worked up as described above for 2-(2-hydroxyphenyl)ethanol. The resulting brownish crystalline product (yield 71 %) was extracted with ether and recrystallised from 95 % ethanol, to give colourless prisms, m.p. 178–179.5° (sublimation above 150°). (Found: C 71.76; H 6.64. Calc. for $C_{18}H_{20}O_4$: C 72.00; H 6.71.) IR (KBr): ν_{max} 1624 (C=C), 1695 (conj. CO), 1726 (CO), 2880 and 2980 (CH-stretching). NMR (DMSO-d_6: δ 1.5–2.2

(8 H, 4 C–CH_2–C), 2.78–3.28 (4 H, 4 CH), 3.67–4.23 (4 H, 2 CH_2–O), 5.75–6.70 (4 H, 4 olefinic H).

3,4-Dihydro-6-hydroxy-5-(3-hydroxypropyl)-1,4-ethenonaphthalene-3-(2'-spirooxolane)-2-(1H)-one (27). Aqueous hydrobromic acid (0.7 ml of a 66 % solution, 12 mmol HBr) was added dropwise to a solution of dimer *26* (0.3 g, 1 mmol) in dioxane (30 ml). After 24 h at room temperature, the reaction mixture was brought to dryness *in vacuo*. The residual brownish oil partially crystallised after being kept in a refrigerator for several months. Recrystallisation from ethyl acetate-hexane gave plates, m.p. 226–228°; yield 17 %. (Found: C 71.66; H 6.46; Br 0.0. Calc. for $C_{18}H_{20}O_4$: C 71.97; H 6.71.) IR (KBr): ν_{max} 1498, 1597 (arom. ring), 1722 (CO), 3245 and 3410 (broad, 2 OH).

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