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Studies on the Autoxidation of *t*-Butyl-substituted Phenols in Alkaline Media. 2.* Reactions of 4,6-Di-*t*-butylguaiacol and Related Compounds

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The courses of the main reactions of 4,6-di-*t*-butylguaiacol (*1*) during alkaline autoxidation are described. Initial oxygenations in the 2- or 4-positions are followed by alkali-promoted rearrangements and conversions of the resulting cyclohexadienone hydroperoxide intermediates. The 3,5-di-*t*-butyl-*o*-quinone formed in one of these conversions undergoes oxidative-alkaline degradation yielding the same fragmentation products as are obtained from *1*.

In the first part of this series the alkaline autoxidation of 4-*t*-butylguaiacol, which serves as a model for "uncondensed" phenolic units in lignins, was studied. The present work is concerned with the autoxidation of 4,6-di-*t*-butylguaiacol and 4-*t*-butyl-2,6-dimethoxyphenol which constitute models for the "condensed" guaiacol and the syringyl-type units, respectively.

* Part 1, see Ref. 1.

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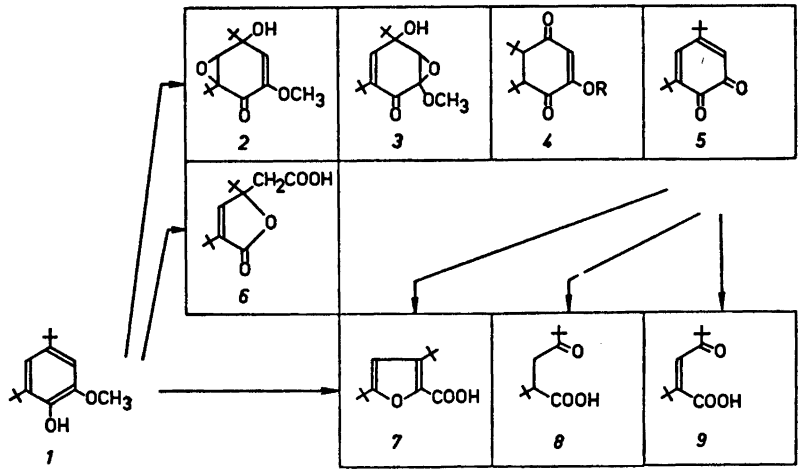
RESULTS AND DISCUSSION

The conditions of the treatments and the results are summarized in Table 1 (see EXPERIMENTAL). The reaction products obtained by autoxidation of 4,6-di-*t*-butylguaiacol (*1*) are depicted in Scheme 1.



Scheme 1. Autoxidation of *1* and *5*. (In this and Schemes 2 – 12, the products isolated are framed).

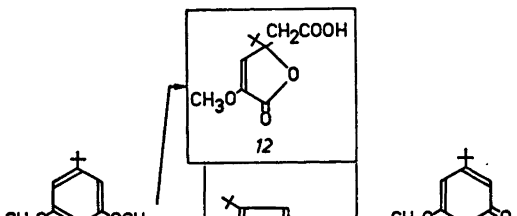
Table 1. Alkaline autoxidation of model compounds. Temperature 40 °C. Alkalinity 0.2 – 0.3 M NaOH. Oxygen consumption 1 – 1.5 mol O_2/mol model compound.

Compound (mol/l)	Solvent EtOH:H_2O	Reaction time, min	Products (Yields, % of theoretical)	Starting material recovered, %
1 (0.1)	3:1	15 × 60	2 (60), *3* (2), *4* (7), *5* (2), *6* (7), *7* (1), *8* (2), *9* (8)	–
2 (0.08)	3:1	14 × 60		90
5 (0.1)	1:3	10	*7* (3), *8* (2), *9* (14), *15* (1), *20* (17), *23*+*24* (2), *25* (2), *26* (8), *27* (3), *28* (2)	–
10 (0.01)	3:1	24 × 60	*12* (8), *13* (20)	50
14 (0.1)	1:3	10	*5* (1), *7* (3), *8* (1), 9 (16), *15* (2), *20* (7), *23*+*24* (2), *25* (8), *26* (14), *26* – ethyl ester (traces), *27* (1), 28 (2)	–
15 (0.08)	1:3	12	*7* (traces), *8* (15), *20* (30), *21*A+*21*B (~10, GC), *25* (10), *26* (traces), *27* (3)	–
16 (0.05)	1:3	10	*7* (10), *9* (15), *25* (20), *28* (20). Yields determined from NMR-spectra.	–
17 (0.03)	1:2	15	*8* (10), *20* (60).	
18 (0.1)	1:3	10	*19*,[a] *25* (60) and other products.	
19 (0.06)	1:3	15		95
24 (0.1)	1:3	30		90

[a] Yield not determined.

Compounds *2*, *3* and *6* have previously been isolated [2,3] after a similar treatment of *1*. The acids *7*, *8* and *9* were also obtained by a similar treatment of 3,5-di-*t*-butyl-*o*-quinone (*5*) which gave six additional compounds as shown in Scheme 6.

Autoxidation of 4-*t*-butyl-2,6-dimethoxyphenol (*10*) (Scheme 2) yielded *12* (*cf.* also Ref. 3) and *13* as main products. The acid *13*, together with three other major products, was also obtained by a similar treatment of 5-*t*-butyl-3-methoxy-*o*-quinone (*11*).[1]

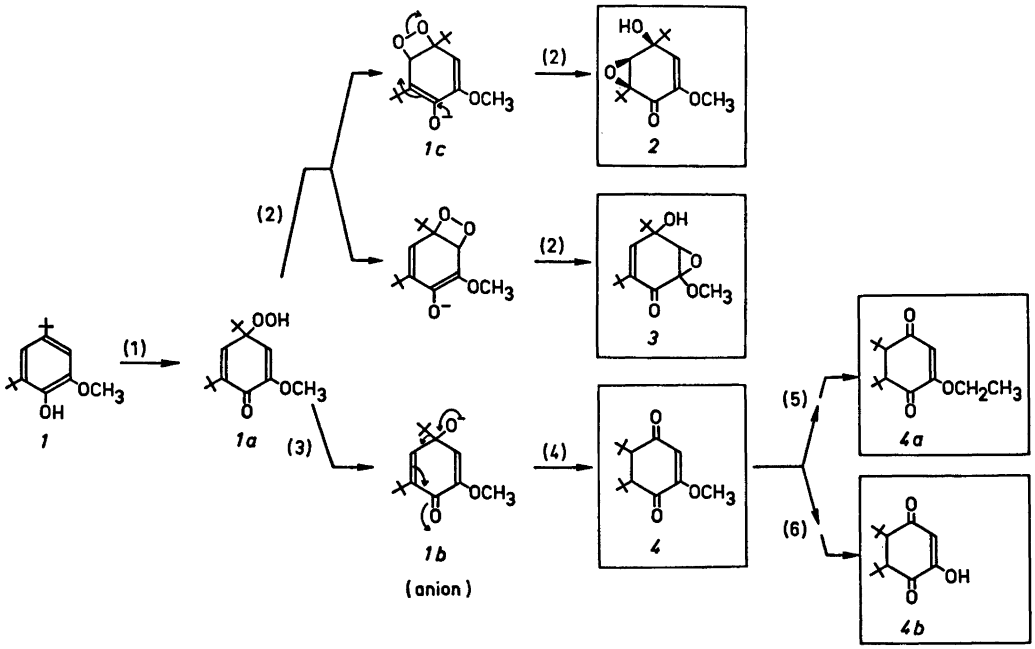


Scheme 2. Autoxidation of *10* and *11*.

Formation of 2, 3 *and* 4. The mechanism of formation of the predominating product *2*, isolated in 60 % yield, and of compounds *3* and *4* is outlined in Scheme 3.

Steps (1) and (2) have been previously suggested.[3,4] Experimental support for these steps has now been provided by the following findings. When the alkaline autoxidation of *1* was carried out in an $^{18}O_2$ atmosphere, the resulting epoxidated quinol *2* contained two atoms of ^{18}O. Furthermore, a structure determination by X-ray crystallography [6] showed that the hydroxyl group and the epoxide ring in *2* bear a *cis* relationship to each other.

These results exclude an alternative mechanism of formation of *2* [2,3] involving alkaline conversion of *1*a into the corresponding hydroxy cyclohexadienone, *1*b, followed by hydrogen



Scheme 3. Formation of *2*, *3* and *4* from *1*: (1) oxygenation,[3,4] (2) intramolecular epoxidations by rearrangement *via* dioxetanes,[3,4] (3) conversion into hydroxy cyclohexadienone,[5] (4) dienone-phenol rearrangement with migration of the 4-*t*-butyl substituent,[5] (5) transetherification by the solvent (ethanol), (6) demethoxylation by alkali.

peroxide oxidation (epoxidation). Formation of *2* through epoxidation of *1*b by *1*a (*cf.* Ref. 7) appears unlikely due to the steric hindrance exerted by the *t*-butyl group.

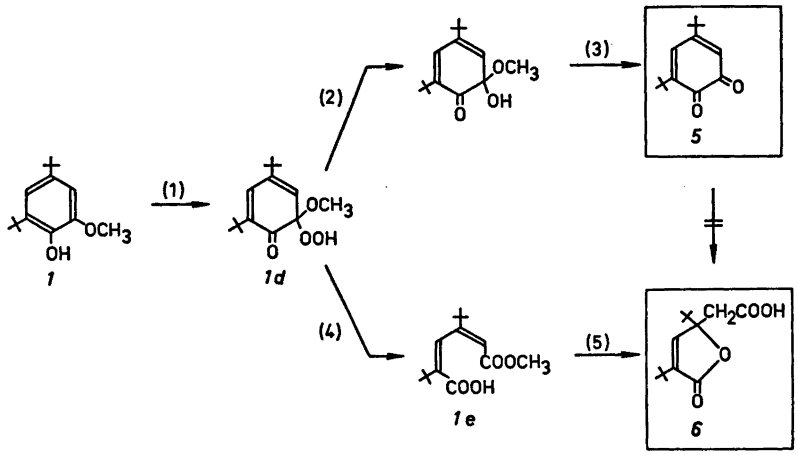
The lower yield of *3* compared to that of *2* indicates that the anion from *1*a preferentially attacks the *t*-butyl-substituted enone moiety (formation of *1*c). However, the lower yield of *3* may also be due to a partial alkaline-oxidative degradation of this compound.

The epoxidated *p*-quinol *2* essentially resists the oxidative-alkaline treatment. This behaviour is in contrast to the extensive degradation of the corresponding product from 4-*t*-butylguaiacol taking place under similar oxidative-alkaline conditions.[1] Obviously, steric factors cause this difference.

The formation of *4* through steps (3) and (4) is formulated in analogy to a previously described [5] anionic dienone-phenol rearrangement involving a 1,2-migration of a *t*-butyl group. The expected final step, enolization of the cyclohexenedione *4* to give the corresponding hydroquinone, is prevented by steric factors (*cf.* Ref. 5).

Transetherification and demethoxylation of *4* [steps (5) and (6)] proceed *via* conjugate 1,4-additions of ethoxide and hydroxide ions, respectively (Michael additions, *cf.* also the alkaline demethoxylation of methoxyquinones [1]). The acidic product *4*b has been previously isolated after alkaline autoxidation of 2,6-di-*t*-butyl-4-methylphenol,[8] 2,6-di-*t*-butyl-*p*-quinone [8] and 4,6-di-*t*-butyl resorcinol,[9] as well as after alkaline treatment of 3,5-di-*t*-butyl-*o*-quinone (*5*) in the absence of oxygen.[5] These reactions involve also alkali-promoted migrations of a *t*-butyl group, similar to step (4) in Scheme 3.

Formation of 5 and 6. The formation of *5* from *1* involves oxidative demethoxylation (Scheme 4). An analogous mechanism *via* a cyclohexadienone hydroperoxide has been previously suggested [10] for the demethoxylation of the isomeric 2,6-di-*t*-butyl-4-methoxyphenol during base-catalyzed autoxidation which gives

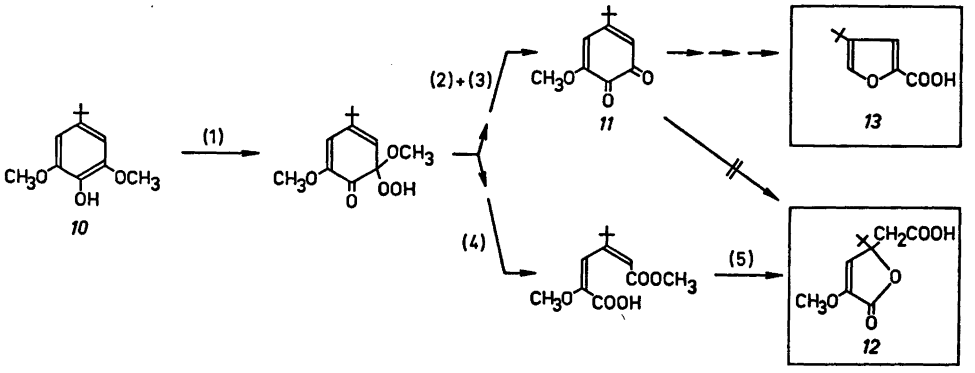


Scheme 4. Formation of *5* and *6* from *1*: (1) oxygenation, (2) alkaline conversion, (3) elimination of methanol (cleavage of hemiketal), (4) ring cleavage by rearrangement *via* dioxetane,[1,3,11] (5) hydrolysis and lactonization.

the corresponding *p*-quinone (*cf.* also Ref. 2). In this instance, the hydroperoxide intermediate could be isolated using mild conditions.[10]

The lactone acid *6* was the main component of the acidic fraction obtained by autoxidation of *1*. Obviously, this acid is formed by oxidative cleavage of the linkage between the carbon atoms carrying the hydroxyl and methoxyl groups of *1*. Two possible routes may be envisaged.[2,3] The initially formed cyclohexadienone hydroperoxide *1*d may undergo rearrangement resulting in ring opening and formation of the monomethyl ester *1*e [step (4)[3] *cf.* also Ref. 11]. The latter is then hydrolyzed before or after lactone formation (5). Alternatively, *6* could arise from the *o*-quinone *5* by oxidative cleavage of the carbon-carbon linkage between the carbonyl groups and subsequent ring closure of the resulting muconic acid.[2,3] However, the latter pathway was excluded by treatment of *5* with oxygen under similar conditions. Only traces of *6* were detected. In contrast to this result, compound *5* has been reported[12] to give *6* in high yield upon treatment with oxygen in a Bu^tOH-Bu^tOK system. This discrepancy is obviously due to the different solvent systems used.

Formation of 12 *and* 13. The reaction routes presented in Scheme 4 also explain the formation of *12* and *13* upon autoxidation of 4-*t*-butyl-2,6-dimethoxyphenol (*10*, Scheme 5).



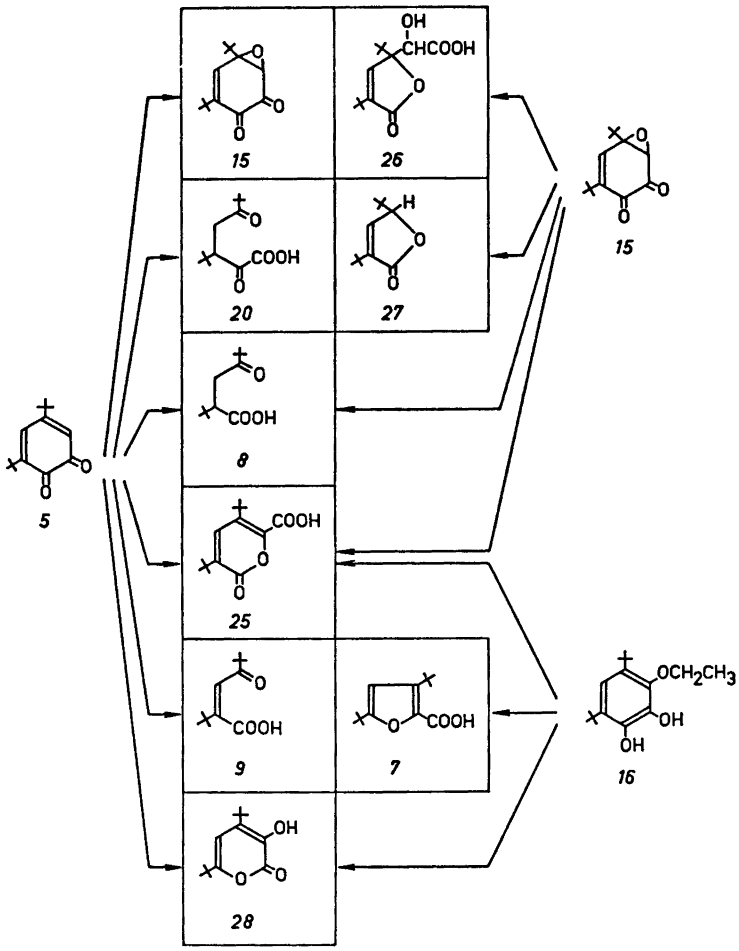
Scheme 5. Formation of *12* and *13* from *10*. (For numbering of reaction steps, see Scheme 4).

Compound *12* corresponds to compound *6* obtained from *1* (Scheme 4), and compound *13* formed *via* *11*[1] corresponds to compound *7* formed *via* *5* (Schemes 7 and 12). Again, *o*-quinone *11* was not converted into the lactone acid *12* during autoxidation. Apparently, the alkaline autoxidation of guaiacol and syringol derivatives to give muconic acid derivatives proceeds *via* internal rearrangement of cyclohexadienone hydroperoxide intermediates rather than *via* oxidative cleavage of *o*-quinoid intermediates.

Formation of 7, 8 *and* 9. The fact that the *o*-quinone *5* was isolated in a small amount (2 %) after autoxidation of *1*, together with the facile oxidation of 5, to 7, 8 and 9 (Scheme 1), indicates that compound *5* is an intermediate in the formation of *7*–*9* from *1*.

In view of the general importance of *o*-quinoid intermediates in the autoxidation of compounds of the guaiacyl type (*cf.* also Ref. 1), all the reaction products isolated after alkaline autoxidation of *5* were investigated. In addition to *7*–*9*, compounds *15*, *20* and *25*–*28* were identified (Scheme 6). Plausible routes for the formation of all identified products are presented in Schemes 7–12. These routes imply that hydrogen peroxide, in addition to oxygen, functions as oxidant (*cf.* also Ref. 1) whereas the formation of the products *2*–*6* from *1* only requires oxygen (Schemes 3 and 4).

The description of the alkaline-oxidative



Scheme 6. Autoxidation of *5*, *15* and *16*.

conversions of *5* is based on the finding that the epoxidated *o*-quinone *15* and the catechol derivative *16*, upon appropriate oxidative treatments, give together all the products obtained from *5* (Scheme 6). *15* and *16* may therefore be considered as possible intermediates in the reactions of *5* (see below).

Formation of the intermediates 15 *and* 16. Compound *15* was isolated in excellent yields after treatment of *5* with hydrogen peroxide or of *14* with oxygen in a 0.2 M solution of sodium hydroxide in aqueous ethanol at 0 °C (Scheme 7). When the oxidative alkaline treatments of *5* and *14* were carried out at 40 °C, the yields of *15* were considerably lower. The oxidations of *5* with hydrogen peroxide and of *14* with oxygen are rapid processes whereas the oxidation of *5* with oxygen under similar conditions proceeds slowly. When *5* was treated with a 0.25 M solution of sodium hydroxide in aqueous ethanol with exclusion of oxygen, a 60 % yield of catechol *14* was obtained. No oxidation products from ethanol were found in the reaction mixture.

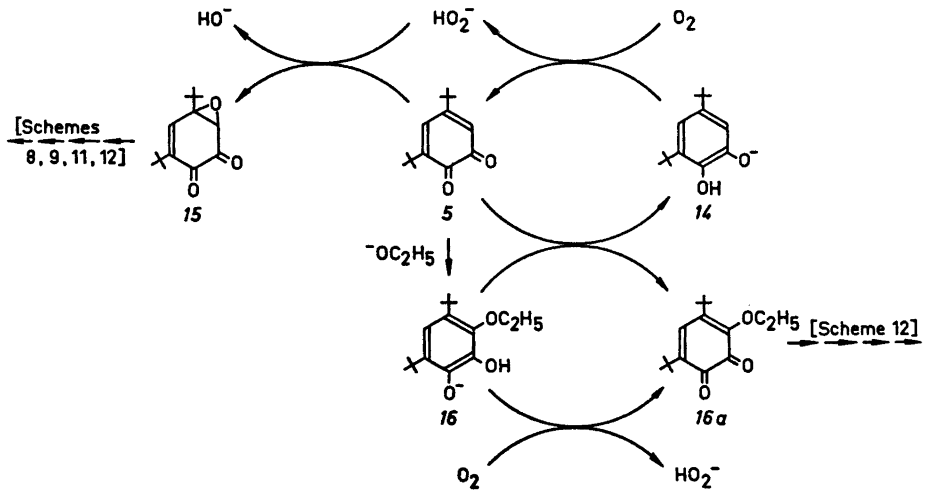
These experimental findings are explained in terms of the redox and addition reactions described in Scheme 7.

The rapid oxidation of catechol *14* with molecular oxygen in alkaline media, yielding *o*-quinone *5*, generates hydrogen peroxide.[13,14] This oxidant reacts rapidly with *5* to give epoxide *15* [15] (*cf.* also Ref. 16).

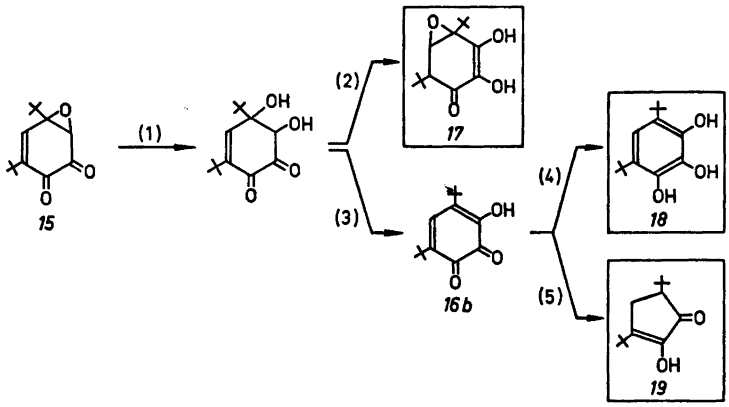
The slow autoxidation of *o*-quinone *5* in alkaline aqueous ethanol is suggested to proceed as follows: Nucleophilic 1,6-addition of ethoxide anions (*cf.* Ref. 17) gives catechol *16* which, however, was not isolated from the reaction mixture. The suggested role of *16* as an intermediate in the autoxidation of *5* is solely indicated by the behaviour towards oxygen in alkali. Autoxidation of *16* gives *16*a and hydrogen peroxide which is available for the conversion of *5* to *15*. Deethoxylation of *16*a gives *16*b which may undergo alkaline-oxidative conversions as outlined in Scheme 12. When the alkaline treatment of *5* is carried out in the absence of oxygen, *16* is obviously oxidized by *5* [18], thereby producing *16*a and *14*. The high yield of the latter compound (60 %) indicates that compound *16*a or the deethoxylation product *16*b is further oxidized by *5*. This reaction has however not been studied so far. The formation of *15* and *16* as intermediates in the oxidative-alkaline degradation of *5* can thus be explained rationally by the competition of hydroperoxide and ethoxide anions for *5*.

In the following sections, the oxidative-alkaline degradations of the intermediates *15* and *16* are briefly described.

Treatment of *15* with alkali in aqueous ethanol in the absence of oxygen afforded



Scheme 7. Redox and addition reactions of *5*.



Scheme 8. Formation of *17*–*19* from *15*: (1) opening of the epoxide ring, (2) rearrangement and tautomerization, (3) elimination of water, (4) reduction by enediols, (5) benzylic acid rearrangement, followed by decarboxylation and tautomerization.[19]

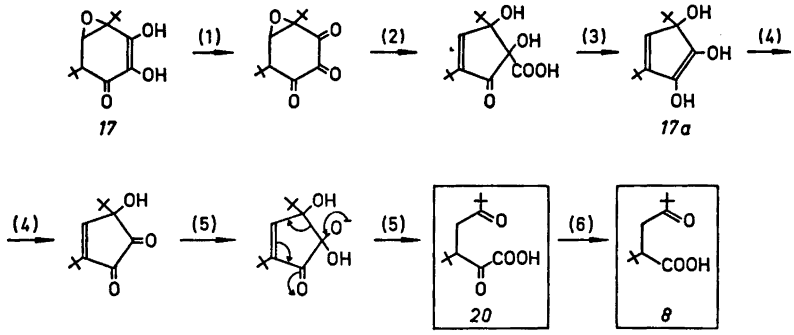
compounds *17*–*19*. The autoxidation of *15* in alkaline media may therefore be preceded by the alkaline (non-oxidative) transformations shown in Scheme 8.

In the presence of oxygen, compounds *17* and *18* undergo further conversions whereas *19* is essentially stable under the conditions used (Table 1).

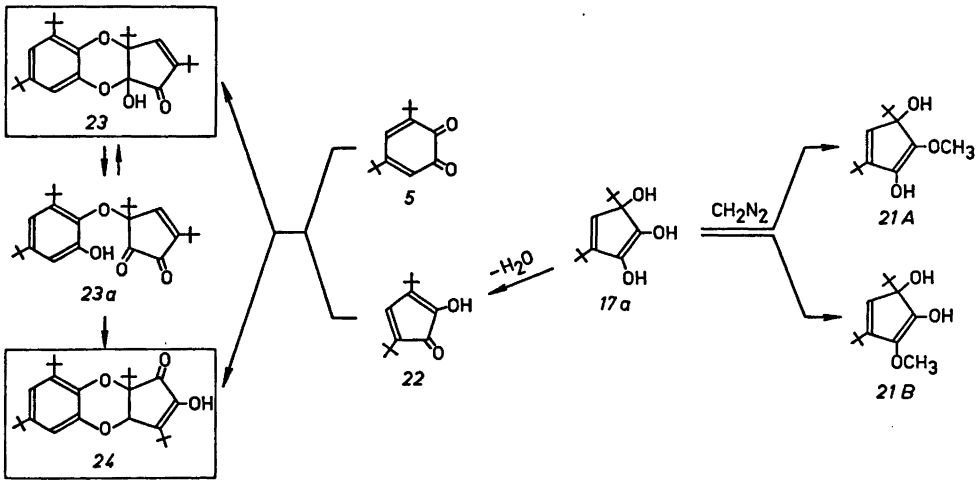
Formation of 20 *and* 8. When *17*, or each of the compounds *5*, *14* and *15*, were treated with alkali in the presence of oxygen, *20* and *8* were formed in varying amounts (Table 1). Compound *17* may therefore be regarded as a possible intermediate in the formation of *20* and *8* from *5*, *14* and *15*. A plausible route for the conversion of *17* into *20* and *8* is outlined in Scheme 9. A similar pathway has been proposed for the formation of the 4-keto acid corresponding to *8* which is obtained on autoxidation of 4-*t*-butylguaiacol.[1]

The validity of the reaction sequence presented in Scheme 9 was supported by demonstrating the intermediary formation of *17*a during the autoxidation of *5*, *14* or *15*. This was achieved in two different ways (Scheme 10).

1. Column chromatography of the reaction mixtures obtained after autoxidation of *5* or *14* gave, among other products, compounds *23* and *24*. The formation of these products is interpreted as a Diels-Alder reaction between *5* acting as "diene" and cyclopentadienone *22* acting as dienophile.[23] *22* is formed from *17*a by elimination of water. The 1,8-addition of



Scheme 9. Formation of *20* and *8* from *17*. (1)=(4) enediol oxidations,[20] (2) benzilic acid rearrangement, (3) decarboxylation, (5) alkaline rearrangement,[21] (6) oxidation by hydrogen peroxide.[21,22]



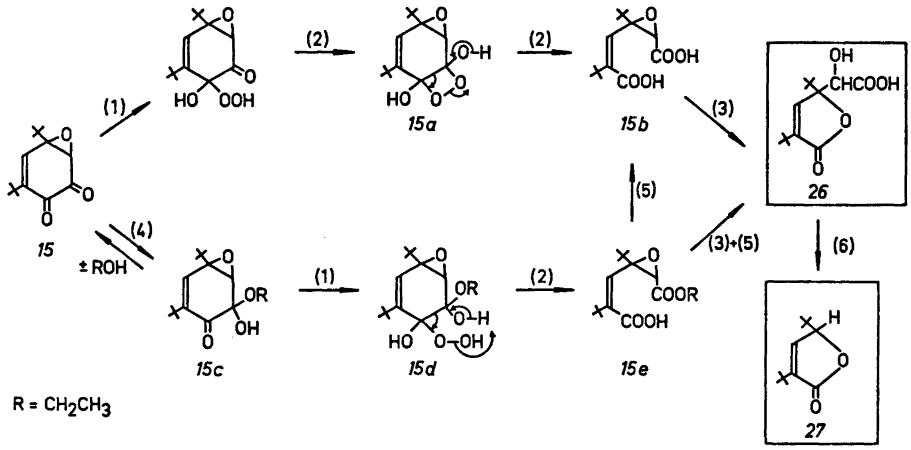
Scheme 10. Trapping of intermediate *17*a (Scheme 9) and its dehydration product *22*.

22 to *5* was demonstrated by reacting authentic *5* and *22* under similar alkaline conditions. A quantitative yield of the dimers *23* and *24* in a ratio of 1:1 was obtained.

Acetylation of the unseparated reaction mixture of *23* and *24* afforded the acetate of *24* only. This shows that *23* easily rearranges probably *via* ring opening by tautomerization (formation of *23*a), followed by intramolecular 1,4-addition of the phenol moiety to the cyclopentenedione part of the molecule. Compound *24* proved stable towards further alkaline-oxidative treatment under the conditions used.

2. GC-MS analysis of the diazomethane-methylated acidic fraction after autoxidation of *15* revealed the presence of two isomeric mono-methyl ethers *21*A and *21*B. Methylation of *17*a is expected to give two isomeric monomethyl ethers due to the enediol nature of this compound.

The oxidative decarboxylation of *20* by the action of hydrogen peroxide [21,22] (Scheme 9) was shown in a separate experiment.



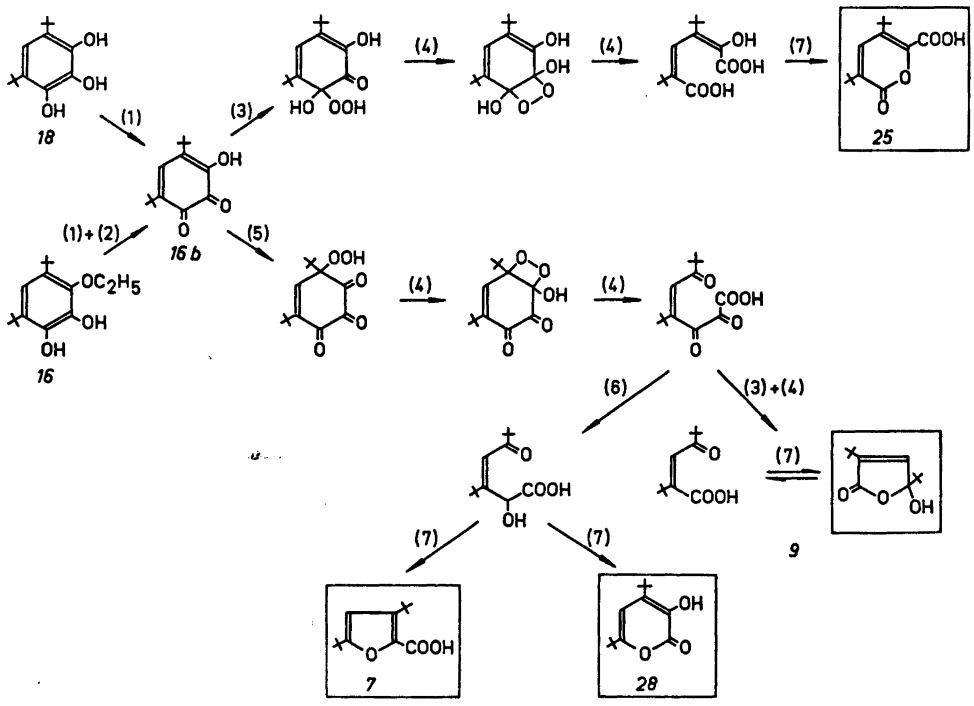
Scheme 11. Formation of *26* and *27* from *15*: (1) addition of hydrogen peroxide, (2) rearrangement, (3) lactone formation with opening of the epoxide ring, (4) addition of ethanol, (5) alkaline hydrolysis of the ester group, (6) alkali-promoted elimination of glyoxylic acid.

Formation of 26 *and* 27. Oxidation of *15* with alkaline hydrogen peroxide in aqueous ethanol at 0 °C gave a 85 % yield of *26*. Treatment of *26* with alkali at 40 °C afforded *27*. These results suggest that *15* is an intermediate, not only in the formation of *8* and *20* (see above) but also in the formation of *26* and *27* from compound *5* (Scheme 6). Two possible pathways for the conversion of *15* into *26* and *27* are outlined in Scheme 11.

Both routes involve addition of hydrogen peroxide to one of the carbonyl groups. The first route then proceeds *via* a dihydroxy dioxetane intermediate (*15*a) which rearranges to give the epoxidated muconic acid *15*b. The second route includes formation of a hemiacetal (*15*c) prior to hydrogen peroxide addition. The hydroperoxy hemiacetal *15*d undergoes a rearrangement with elimination of water and formation of the corresponding epoxidated muconic acid half ester (*15*e). Compound *15*e is hydrolyzed before or after cyclization. The latter reaction entails the opening of the epoxide ring.

Some support has been provided indicating that the conversion of *15* into *26* may, to a certain extent, follow the second route: The facile acetalization of *15* was shown by dissolving this compound in chloroform-ethanol (20:1) and isolating *15*c in a quantitative yield (^{1}H NMR). Furthermore, autoxidation of *14* in an alkaline solution containing ethanol and water (1:3) gave traces of the ethyl ester of *26* together with *26*, *27* and many other compounds (*cf.* also Ref. 24 and 25). Apparently, the ester group, to a certain extent, resists alkaline hydrolysis. The methyl ester of *26* has previously been isolated [25] in 20 % yield after treatment of compound *5* with alkaline (0.1 M Na_2CO_3) hydrogen peroxide in aqueous methanol.

Formation of 7, 9, 25 *and* 28. Autoxidation of *16* gave the lactones *9*, *25* and *28*, and the furoic acid *7* (Scheme 12). These compounds were



Scheme 12. Formation of *7*, *9*, *25* and *28* from *16*: (1) enediol oxidations, (2) alkaline deethoxylation, (3) addition of hydrogen peroxide, (4) hydroperoxide rearrangements *via* dioxetanes, (5) oxygenation, (6) decarboxylation, (7) cyclizations.

also present in the reaction mixtures obtained on autoxidation of *5* (Scheme 6). Compound *25* was also formed upon autoxidation of *14*, *15* or *18*. When treated under suitable conditions, compound *18* afforded *25* in high yield together with varying amounts of *19* (*cf.* also Ref. 19).

Plausible routes leading from compounds *16* and *18* to *7*, *9*, *25* and *28* are presented in Scheme 12.

The oxidative ring cleavages described in this Scheme are suggested to proceed by rearrangement *via* dioxetane intermediates. However, as in the oxidation of *15* (Scheme 11), an alternative mechanism of ring cleavage, involving rearrangement of a hydroperoxy hemiacetal intermediate, may also be operative to a certain extent (*cf.* also Ref. 1).

Scheme 12 can also be used to explain the following findings:

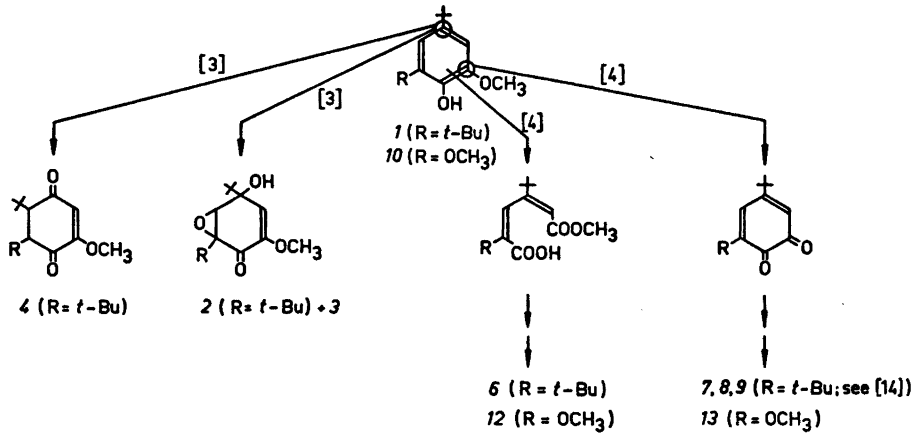
1. Products corresponding to *7*, *9*, *25* and *28* are obtained upon a similar autoxidation of 3-methoxy-5-*t*-butyl-*o*-benzoquinone (*11*) arising *via* oxygenation of 4-*t*-butylguaiacol[1] or by oxidative demethoxylation of 4-*t*-butyl-2,6-dimethoxyphenol (*10*, Scheme 5). The formation of these products has been formulated analogously,[1] 3-hydroxy-5-*t*-butyl-*o*-benzoquinone being the quinoid intermediate instead of *16*b.

2. The hydroxylactone *9* has previously been obtained by autoxidation of *5* in *t*-butanol[12] and of 2,6-dimethoxy-3,5-di-*t*-butylphenol in aqueous ethanol.[3] The formation of *9* from the latter substrate should also proceed *via* *16*b arising by oxidative demethoxylation (*cf.* also behaviour of *10*, Scheme 5), followed by alkaline demethoxylation.[1]

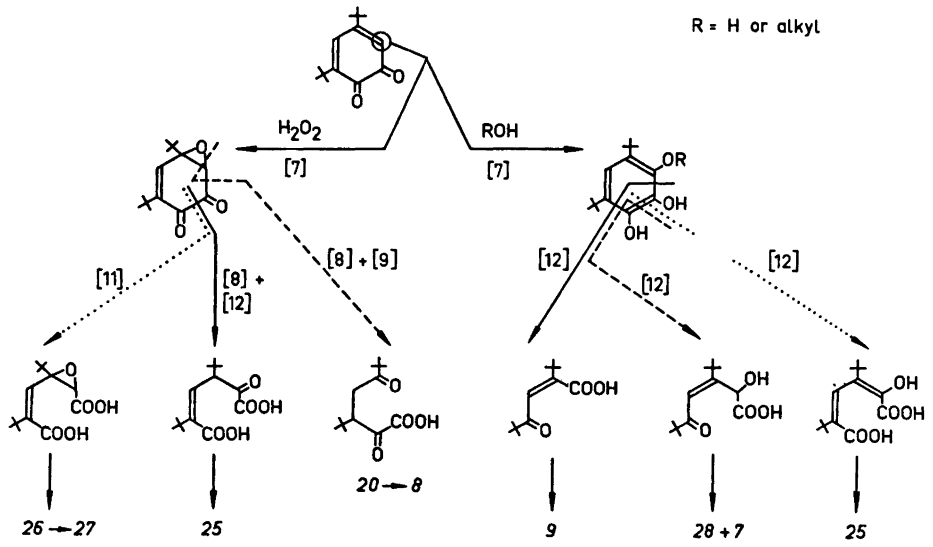
CONCLUSIONS

The reaction taking place during the autoxidation of 4,6-di-*t*-butylguaiacol (*1*) can be divided into two categories: The first includes oxygenations in the 2 and 4-positions followed by alkali-promoted rearrangements and conversions of cyclohexadienone hydroperoxide intermediates (Schemes 3 and 4). The second comprises nucleophilic additions of hydroperoxy, hydroxy and alkoxy anions in the 6- (originally 3-) position of the *ortho*-quinone intermediate (Scheme 7), followed by alkaline and oxidative conversions and degradations of the addition products (Schemes 8, 9, 11 and 12). The courses of the alkaline-oxidative transformations of *1* and of intermediate *5* are summarized in Schemes 13 and 14, respectively. The figures within brackets in these schemes refer to previous schemes in the text. The arrows indicate the sites of alkline-oxidative attack, ring cleavage and also, in the case of Scheme 14, fragmentation.

The other compound investigated, 4-*t*-butyl-2,6-dimethoxyphenol (*10*), reacts in a similar fashion, the 2-position constituting the main site of primary oxygenation (Schemes 5 and 13).



Scheme 13. Course of degradation of *1* (summary).



Scheme 14. Course of degradation of *5* (summary).

EXPERIMENTAL

Materials

Syntheses of model compounds. The following compounds were prepared as previously described: *1*,[26] *10*,[27] *11*,[1] *18*,[28] *19* [21] and *22*.[29]

3,5-Di-t-butyl-o-quinone (5). A method described for the synthesis of 4-methyl-*o*-quinone [30] from 4-methylcatechol was adopted. Sodium metaperiodate (50 mmol) in water (200 ml) was added to a cooled solution (+5 °C) of 3,5-di-*t*-butylcatechol (50 mmol) in 60 % acetic acid (300 ml). The reaction mixture was extracted with methylene chloride (2 × 400 ml) after 1 min. The coloured extract was washed free of acid, dried with sodium sulfate and evaporated to yield 11 g of crude material. Crystallization from light petroleum (40–60 °C) yielded dark red needles (9 g, 82 %), m.p. 116–117 °C (lit.[24] 113–114 °C).

4,5-Epoxy-6-oxo-2,4-di-t-butylcyclohex-2-enone (15). 3,5-Di-*t*-butyl-catechol (*14*) (20 mmol), dissolved in a 0.2 N solution of sodium hydroxide containing ethanol-water (3:1) (200 ml), was autoxidized at 0 °C. The reaction mixture was neutralized with carbon dioxide after 20 min (oxygen consumption: 1.2 equiv.) diluted with water and extracted with methylene chloride. The yellow extract was dried with sodium sulfate and evaporated to yield crude material (4.7 g) which was dissolved in benzene (20 ml). After concentration under reduced pressure, light petroleum (20 ml) was added precipitating pale yellow needles (3.1 g, 65 %). For spectroscopic data and elemental analyses, see Table 3 and data below.

4,6-Di-t-butyl-3-ethoxycatechol (16). 3-Ethoxycatechol [31] (1.0 mmol) in acetic acid (2 ml) and *t*-butanol (3 ml) were treated with sulfuric acid (0.85 ml) at 20 °C. The reaction mixture was kept at room temperature for 24 h. After dilution with water, the solution was extracted with methylene chloride. Evaporation of the dried (Na_2SO_4) extract yielded 0.27 g of crude material. Recrystallization from light petroleum (40–60 °C) gave white crystals (0.18 g, m.p. 151–153 °C). Anal. $C_{16}H_{26}O_3$: C, H, O. ^1H NMR (60 MHz, $CDCl_3$): δ 1.34 (s, 9 H, *t*-Bu), 1.37 (s, 9 H, *t*-Bu), 1.42 (t, 3 H, CH_3, *J* 7.5), 3.93 (q, 2 H, CH_2, *J* 7.5), ~5.15 (broad s, 1 H, OH), ~5.50 (broad s, 1 H, OH), 6.73 (s, 1 H, ar).

Methods

Autoxidation of model compounds. The treatment of the model compounds with oxygen and the work-up procedure were carried out as previously [1] described. The conditions and results are given in Table 1.

Autoxidation of 4,6-di-t-butylguaiacol (1) with $^{18}O_2$. The reaction was performed under the conditions given in Table 1 except that $^{18}O_2$ mixed with N_2 (~80 vol %) was used as oxidant. The resulting epoxide (*2*) was identified by GC-MS analysis (see p. 000).

Autoxidation of 3,5-di-t-butyl-o-quinone (5) at 0 °C. Compound *5* (10 mmol) was autoxidized in a 0.2 M solution of sodium hydroxide in ethanol-water (4:1) (100 ml). 1.2 equivalents of oxygen were consumed within 8 h. The reaction mixture was not investigated in detail. The

presence of *15* in the neutral fraction was shown by TLC.

Autoxidation of 3,5-di-t-butylcatechol (14) at 0 °C, see preparation of compound *15* above.

Oxidation of model compounds with alkaline hydrogen peroxide. The oxidation of model compounds with alkaline hydrogen peroxide was carried out in an atmosphere of nitrogen. The work-up procedure was essentially the same as that described for the autoxidation experiments.[1] The extractions were carried out with methylene chloride instead of ether. The conditions and results are given in Table 2.

Alkaline treatment of model compounds. All treatments were carried out in an atmosphere of nitrogen.

Table 2. Oxidation of model compounds with alkaline hydrogen peroxide. Alkalinity 0.2–0.3 M NaOH. Temperature 40 °C.

Compound (mol/l)	Solvent EtOH:H_2O	Equivalents of H_2O_2	Reaction time, min	*t*, °C	Products (Yields % of theoretical)
5 (0.1)	4:1	1.2	10	0	*15* (55), *26* (20)
15 (0.1)	4:1	1.5	10	0	*26* (85)
17 (0.1)	1:1	2	30	40	*8* (80), *20*[a]
20 (0.1)	1:1	2	120	40	*8* (60)

[a] Yield not determined.

Table 3. ^{1}H NMR of products isolated from alkaline autoxidation of *1*, *5*, *10*, *14*, *15* and *16*. Types of protons: ac, acetyl; ar, aromatic; es, ester; et, ether; ol, olefinic.

Compound	δ (*t*-Bu) (s, 9 H)	δ (Me) (s, 3 H)	δ other protons
2	1.02, 1.11	3.58 (et)	3.74 (d, 1 H, CH), 5.18 (d, 1 H, ol), $J_{CH,ol}$ 2.7 Hz, 2.44 (s, 1 H, OH)
3	0.99, 1.20	3.55 (et)	3.85 (d, 1 H, CH), 6.10 (d, 1 H, ol), $J_{CH,ol}$ 2.7 Hz, 2.27 (s, 1 H, OH)
4 R = CH_3	0.95[a]	3.75 (et)	3.68 (s, 1 H, CH), 3.76 (s, 1 H, CH), 5.93 (s, 1 H, ol)
4 R = C_2H_5	0.95[a]		1.43 (t, 3 H, CH_3), 3.96 (q, 2 H, CH_2), J_{CH_3,CH_2} 7.3 Hz, 2.67 (s, 1 H, CH), 2.75 (s, 1 H, CH), 5.93 (s, 1 H, ol)
6[b]	0.97, 1.22	3.57 (es)	3.01 (A) and 2.73 (B) [CH_2; AB; J_{AB} 14.0 Hz]
7[b]	1.19, 1.26	3.82 (es)	6.03 (s, 1 H, ol)
8[b]	1.00, 1.15	3.63 (es)	2.30–3.30 (m, 3 H, CH+CH_2)
9[b]	1.16, 1.20	3.80 (es)	6.43 (s, 1 H, ol)
9 (lactone)	1.02, 1.23		6.76 (s, 1 H, ol), 3.32 (broad s, 1 H, OH)
12	1.00	3.75 (et)	2.89 (s, 2 H, CH_2), 6.07 (s, 1 H, ol), 9.37 (broad s, 1 H, OH)
15	1.10, 1.20		3.80 (d, 1 H, CH), 7.07 (d, 1 H, ol), $J_{CH,ol}$ 0.9 Hz
20[b]	0.99, 1.12	3.90 (es)	2.60–3.40 (m, 2 H, CH_2), 3.50–3.80 (q, 1 H, CH)
23	1.08, 1.18 1.27[a]		6.83 (s, 2 H, ar), 7.08 (s, 1 H, ol), 4.09 (s, 1 H, OH)
24	0.97, 1.25 1.38, 1.44		5.00 (s, 1 H, CH), 6.87 (broad s, 2 H, ar), 5.65 (broad s, 1 H, OH)
25	1.35[a]		7.40 (s, 1 H, ol), 9.70 (broad s, 1 H, OH)
26	1.07, 1.20		4.68 (s, 1 H, CH), 7.06 (s, 1 H, ol), 5.15 (s, 2 H, OH)
27	0.95, 1.25		4.48 (d, 1 H, CH), 6.92 (d, 1 H, ol) $J_{CH,ol}$ 1.5 Hz
28	1.25, 1.33		6.00 (s, 1 H, ol), 6.45 (s, 1 H, OH)

[a] 18 H. [b] Methyl ester.

Alkaline treatment of 5. Compound *5* (5 mmol) was treated with a 0.25 M solution of sodium hydroxide in ethanol-water (3:1) (100 ml) at 40 °C for 30 min. 3,5-Di-*t*-butylcatechol (*14*) was the main product (~60 %, determined from the ^{1}H NMR spectrum of the neutral fraction).

Alkaline treatment of 15. Compound *15* (6 mmol) was treated with a 0.3 M solution of sodium hydroxide in ethanol-water (4:1) (100 ml) at 40 °C for 25 min. The reaction mixture consisted of the acidic products *17* (30 %) and *20* (10 %) and the neutral products *18* (35 %) and *19* (10 %). The yields were determined from ^{1}H NMR spectra of the crude acidic and neutral fractions. The yield of *17* was increased to 70 % by treating *15* with a stronger alkaline solution (3 M sodium hydroxide) containing ethanol-water (3:1) under otherwise identical conditions.

Alkaline treatment of a mixture of 5 *and* 22. Compound *5* (0.5 mmol) and compound *22* (0.5 mmol) were dissolved in a 0.3 M solution of sodium hydroxide containing ethanol-water (4:1) (10 ml) and kept at 40 °C. The solution became colourless within 15 min. After neutralization (CO_2) and dilution with water (50 ml), a white precipitate (0.17 g, 80 %) was formed. The ^{1}H NMR spectrum of this product revealed the presence of *23* and *24* in an approximate ratio of 1:1. Acetylation of this mixture gave *24*-acetate (yield 91 %).

Chromatography. The preparative separations by column or thin-layer chromatography and the gas chromatography separations combined with mass spectral analyses were carried out as previously [1] described.

Product identification

The reaction products were identified by usual spectrometric methods (types of instruments used are given in Ref. 1). The ^{1}H NMR data are presented in Table 3. IR, UV and MS data are given in the following. Only mass fragments (max. 8) with $m/e > 100$ and relative intensities > 10 % of the base peak are included.

5,6-Epoxy-4-hydroxy-2-methoxy-4,6-di-t-butylcyclohex-2-enone (*2*). m.p. 102–103 °C. Anal. $C_{15}H_{24}O_4$: C, H, O, MS *m/e* (rel. int.): 212, (M–56, 45), 211 (M–57, 100), 194 (M–74, 10), 179 (M–89, 10), 156 (95), 151 (30), 143 (30), 141 (30). IR (KBr): 3505 (s, OH), 3490 (m, OH), 1695 (s, C=O), 1635 (m, C=C–C=O). UV [MeOH (ε)]: 272 (3400).

2,3-Epoxy-4-hydroxy-2-methoxy-4,6-di-t-butylcyclohex-5-enone (*3*), m.p. 100–100.5 °C. Anal. $C_{15}H_{24}O_4$: C, H, O. MS *m/e* (rel. int.): 240 (M–28, 15), 239 (M–29, 90), 212 (M–56, 90), 211 (M–57, 65), 209 (85), 183 (25), 179 (75), 153 (100). IR (KBr): 3470 (m, OH), 1685 (s, C=O). UV [EtOH (ε)]: 228 (16.000).

1-Methoxy-4,5-di-t-butyl-cyclohex-1-enedi-3,6-one (4, $R = CH_3$), m.p. 150 °C. MS *m/e* (rel. int.): 171 (M–81, 10), 140 (M–112, 100), 125 (15). IR (KBr): 1685 (s, C=O), 1655 (s, C=C–C=O), 1610 (C=C–C=O). UV [MeOH (ε)]: 271 (–).

1-Ethoxy-4,5-di-t-butyl-cyclohex-1-enedi-3,6-one (4, $R = C_2H_5$), m.p. 95–97 °C. Anal. $C_{16}H_{26}O_3$: C, H. MS *m/e* (rel. int.): 154 (M–112, 100), 126 (35). IR (KBr): 1680 (s. C=O), 1650 (s, C=C–C=O), 1600 (s, C=C–C=O). UV [EtOH (ε)]: 274 (10 750).

Methyl 2,5-dihydro-5-oxo-2,4-di-t-butylfuran-2-acetate (methyl ester of 6), m.p. 67–69 °C. Anal. $C_{15}H_{24}O_4$: C, H, O. MS *m/e* (rel. int.):* 212 (M–56, 100), 197 (M–71, 75), 153 (M–115, 38), 137 (10), 109 (30), IR (KBr): 1745 (s, C=O), 1735 (s, C=O), 1640 (w, C=C–C=O). UV [MeOH (ε)]: 215 (sh, –).

Methyl 3,5-di-t-butyl-2-furoate(methyl ester of 7), amorphous: Anal. $C_{14}H_{22}O_3$: C, H, O. MS *m/e* (rel. int.): 238 (10), 223 (100), 207 (10), 191 (20), 165 (20). IR ($CHCl_3$): 1710 (s, C=O), 1585 (m, C=C), 1520 (m, C=C).

Methyl 5,5-dimethyl-2-t-butyl-4-oxohexanoate (methyl ester of 8), amorphous. MS *m/e* (rel. int.): 197 (M–31, 10), 171 (M–57, 100), 143 (M–85, 40), 125 (15), 111 (80). IR ($CHCl_3$): 1730 (s, C=O), 1710 (s, C=O).

Methyl 5,5-dimethyl-4-oxo-2-t-butyl-hex-2-enoate (methyl ester of 9), amorphous. Anal. $C_{13}H_{22}O_3$: C, H, O. MS *m/e* (rel. int.): 195 (M–31, 10), 170 (M–56, 100), 169 (M–57, 65), 155 (85), 141 (20), 109 (20). IR ($CHCl_3$): 1725 (s, C=O), 1685 (m, C=O), 1610 (m, C=C–C=O).

α,γ-Di-t-butyl-γ-hydroxy-Δ-α,β-butenolide (lactone of 9), m.p. 98–100 °C. Anal. $C_{12}H_{20}O_3$: C, H, O. MS *m/e* (rel. int.): 156 (M–56, 100), 155 (M–57, 20), 141 (M–71, 40), 138 (10), 125 (10), 109 (15). IR (KBr): 3460 (s, OH), 1730 (s, C=O), 1635 (w, C=C–C=O). UV [EtOH (ε)]: 212 (9700).

2,5-Dihydro-5-oxo-4-methoxy-2-t-butylfuran-2-acetic acid (*12*), m.p. 144–145 °C. Anal. $C_{11}H_{16}O_5$: C, H, O. MS *m/e* (rel. int.): 172 (M–56, 100), 127 (M–101, 50). IR (KBr): 1765 (s, C=O), 1690 (s, C=O), 1655 (s, C=C–C=O). UV [EtOH (ε)]: 227 (12 300).

3,4-Epoxy-3,4-dihydro-4,6-di-t-butyl-1,2-benzoquinone (*15*), m.p. 100–101 °C. Anal. $C_{14}H_{20}O_3$: C, H, O. MS *m/e* (rel. int.): 208 (M–28, 20), 207 (M–29, 25), 193 (M–43, 95), 180 (M–56, 100), 165 (75), 151 (25), 150 (55), 149 (17). IR (KBr): 1730 (s, C=O), 1680 (s, C=O), 1610 (w, C=C–C=O). UV [EtOH (ε)]: 247 (4600).

Methyl 6,6-dimethyl-3-t-butyl-2,5-dioxoheptanoate (methyl ester of 20), m.p. 89–90 °C. Anal. $C_{14}H_{24}O_4$: C, H, O. MS *m/e* (rel. int.): 238 (M–18, 10), 223 (M–33, 35), 197 (M–59, 100), 169 (20), 151 (25), 143 (20), 113 (15). IR (KBr): 1735 (s, C=O), 1715 (s, C=O), 1685 (s, C=O).

9a-Hydroxy-3a,9a-dihydro-2,3a,5,7-tetra-t-butyl-1H-cyclopenta-[b] [*1,4*]*benzodioxin-1-one*

* Yield not determined.

(23), m.p. 196–197 °C. MS *m/e* (rel. int.): 428 (M, 55), 221 (M–207, 50), 207 (M–221, 45), 165 (100), 152 (60), 151 (35), 137 (45). IR (KBr): 3410 (s, OH), 1725 (s, C=O), 1605 (w, C=C–C=O), 1585 (m, aromatic C=C).

2-Hydroxy-3a,9a-dihydro-3,6,8,9a-tetra-t-*butyl-1H-cyclopenta*-[b] *[1,4]benzodioxin-1-one (24)*, m.p. 192–194 °C. Anal. $C_{27}H_{40}O_4$: C, H, O. IR (KBr): 3360 (s, OH), 1705 (s, C=O), 1645 (m, C=C–C=O), 1580 (m, aromatic C=C). UV [Ethyl ether (ε)]: 262 (10 000).

3,5-Di-t-*butyl-6-carboxy-2H-pyran-2-one (25)*, m.p. 188–190 °C. MS *m/e* (rel. int.): 252 (M, 35), 237 (M–15, 20), 209 (M–43, 95), 195 (M–57, 40), 193 (35), 192 (35), 178 (35), 167 (100). IR (KBr): 2800–2500 (m, OH), 1754 (s, C=O), 1660 (s, C=O), 1630 (m, C=C–C=O), 1565 (s, C=C–C=O).

2,5-Dihydro-5-oxo-2,4-di-t-butylfuran-2-glycolic acid (26), m.p. 137–139 °C. Anal. $C_{14}H_{22}O_5$: C, H, O. MS *m/e* (rel. int.): 209 (M–61, 15), 197 (M–73, 100), 169 (M–104, 30), 165 (M–105, 40), 151 (35), 129 (15), 125 (25), 113 (65). IR (KBr): 3500–3200 (m, OH), 1740–1700 (s, C=O), 1630 (w, C=C–C=O). UV [MeOH (ε)]: 215 (9200).

α,γ-Di-t-*butyl-Δ^{α,β}-butenolide (27)*, m.p. 96–97 °C. Anal. $C_{12}H_{20}O_2$: C, H, O. MS *m/e* (rel. int.): 181 (M–15, 10), 140 (M–56, 80), 125 (M–71, 100). UV [MeOH (ε)]: 211 (12 300).

3-Hydroxy-4,6-di-t-*butyl-2H-pyran-2-one (28)*, m.p. 121–122 °C. Anal. $C_{13}H_{20}O_3$: C, H, O. MS *m/e* (rel. int.): 224 (M, 30), 209 (M–15, 100), 181 (M–43, 20). IR (KBr): 3335 (s, OH), 1680 (s, C=O), 1640 (s, C=C–C=O), 1555 (m, C=C–C=O). UV [EtOH (ε)]: 305 (9300).

Further identification of products and intermediates

Mass spectrum of *2* obtained in $^{18}O_2$ atmosphere: Mass fragments having *m/e* > base peak and rel. int. > 5 % are listed. *m/e* (% rel.int.): 221 (14), 216 (5), 215 (10), 213 (5), 212 (7), 211 (6), 210 (10), 208 (5), 196 (8), 195 (10), 193 (7), 185 (12), 184 (100). Mass spectrum of *2* obtained in $^{16}O_2$ atmosphere: *m/e* (% rel. int.): 221 (14), 212 (10), 211 (22), 209 (8), 208 (22), 207 (7), 194 (9), 193 (22), 182 (10), 181 (40), 180 (100).

High resolution mass spectrometry of *2* ($^{16}O_2$) showed that the fragment with mass number 212 is $C_{11}H_{16}O_4$ (M–C_4H_8). (Calc.: *m/e* = 212.1048. Found: *m/e* = 212.1035). The corresponding fragment from *2* ($^{18}O_2$), *m/e* = 216, was found and it is therefore concluded that two atoms of ^{18}O were incorporated during autoxidation (Scheme 3).

Treatment of 15 *with diazomethane. 15* was treated with diazomethane in ether to give a quantitative yield of *2,4-di-t-butyl-4,5-epoxy-6-spiroepoxy-cyclohex-2-enone*, m.p. 83–85 °C. Anal. $C_{15}H_{22}O_3$: C, H, O. IR (KBr): 1675 (s, C=O), 1620 (s, C=C–C=O). UV [MeOH, (ε)]: 252 (4850). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.05 (s, 9 H, *t*-Bu), 1.18 (s, 9 H, *t*-Bu), 3.18 and 3.44 (dd, 2 H, CH_2, J_{gem} 6.6 Hz), 3.38 (d, 1 H, CH, *J* ~ 1 Hz), 7.12 (d, 1 H, ol, *J* ~ 1 Hz). The same compound was isolated after autoxidation of *5*, methylation and separation of the reaction mixture.

2,3-Dihydroxy-4,5-epoxy-4,6-di-t-*butylcyclohex-2-enone (17)*, UV [MeOH, (ε)]: 271 (9000). ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.97 (s, 9 H, *t*-Bu), 1.14 (s, 9 H, *t*-Bu), 2.70 (d, 1 H, CH, *J* 1.5 Hz), 4.02 (d, 1 H, CH, *J* 1.5 Hz), 7.10 (broad s, 2 H, OH, exchangeable). Acetylation of *17* followed by methylation (diazomethane) gave two isomeric acetylated monomethyl ethers.

Separation by preparative TLC afforded: *2-Acetoxy-4,5-epoxy-3-methoxy-4,6-di*-t-*butylcyclohex-2-enone*, colourless crystals, m.p. 82–85 °C (light petroleum). Anal. $C_{17}H_{26}O_5$: C, H, O. IR (KBr): 1765 (s, C=O), 1710 (s, C=O), 1690 (s, C=C–C=O), 1625 (m, C=C–C=O). UV [EtOH (ε)]: 253 (10 700). ^{1}H NMR (60 MHz, $CDCl_3$): 0.97 (s, 9 H *t*-Bu), 1.13 (s, 9 H, *t*-Bu), 2.19 (s, 3 H, ac), 4.05 (s, 3 H, OMe), 2.87 (d, 1 H, CH, *J* 3 Hz), 4.05 (d, 1 H, CH, *J* 3 Hz).

2-Acetoxy-5,6-epoxy-3-methoxy-4,6-di-t-*butylcyclohex-2-enone*, colourless crystals, m.p. 100 °C (light petroleum). Anal. $C_{17}H_{26}O_5$: C, H, O. IR (KBr): 1770 (s, C=O), 1705 (s, C=O), 1695 (s, C=C–C=O), 1635 (m, C=C–C=C). UV [EtOH (ε)]: 248 (12200). ^{1}H NMR (60 MHz, $CDCl_3$): 1.00 (s, 9 H, *t*-Bu), 1.20 (s, 9 H, *t*-Bu), 2.20 (s, 3 H, ac), 3.96 (s, 3 H, OMe), 2.28 (d, 1 H, CH, *J* 3 Hz), 4.06 (d, 1 H, CH *J* 3 Hz).

1,3-Dihydroxy-2-methoxy-1,4-di-t-*butylcyclopentadiene (21A) and 1,2-dihydroxy-3-methoxy-1,4-di*-t-*butylcyclopentadiene (21B)*. GC-MS analysis (molecular ion and mass fragments having *m/e* > 100 and rel. int. > 10 % of the base peak are given):

*17*a-monomethyl ether (form 1): 240 (M, 5), 238 (M–2, 10), 223 (M–17, 55), 191 (M–49, 10), 183 (M–57, 100), 170 (20), 169 (15), 165 (17), 155 (20), 141 (35), 127 (27), 109 (55).

*17*a-monomethyl ether (form 2): 240 (M, 7) 223 (M–17, 15), 183 (M–57, 100), 165 (20), 141 (30), 127 (25), 109 (40). On the basis of the mass spectra, however, it was not possible to attribute structures *21*A and *21*B to forms 1 and 2.

2-Acetoxy-3a,9a-dihydro-3,6,8,9a-tetra-t-*butyl-1H-cyclopenta*[b] *[1.4]-benzodioxin-1-one (acetate of 24)*. In addition to the ^{1}H NMR data given in Table 3, the structure of *24* was confirmed by the ^{13}C NMR spectrum (20 MHz, $CDCl_3$) of *24*-acetate: δ 195.49 (C 1), 166.73 (C=O in acetate), 161.79 (C 3), 148.97, 145.27, 144.96, 139.75, 137.98 (C 2, C 5, C 6, C 7, C 8), 116.01, 112.59 (C 4 a, C 8 a), 84.22 (C 3 a), 74.80 (C 9 a), 38.26, 34.55, 34.36, 34.05 (–C–)

in *t*-Bu), 31.41, 30.15, 28.74 and 25.87 (CH_3 in *t*-Bu), 20.26 (CH_3 in acetate). The location of *t*-butyl groups at the carbon atoms 6 and 8 in the benzodioxin ring is uncertain. They may possibly be linked to carbon atoms 5 and 7.

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