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Studies on the Autoxidation of *t*-Butyl-substituted Phenols in Alkaline Media. 1. Reactions of 4-*t*-Butylguaiacol

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The course of the alkaline autoxidation of 4-*t*-butylguaiacol is described. Initial oxygenations in the 4- and 6-positions are followed by alkaline-oxidative conversions of the resulting intermediates, *viz.* an epoxidated hydroxycyclohexadienone and an *o*-quinone, into carboxylic acids and lactones. Oxidative coupling to give a dimer competes with the degradation routes.

Numerous studies on the autoxidation of organic compounds [1] in alkaline media have revealed that the process proceeds *via* peroxy anions (R—O—O⁻). The formation of these important intermediates may be formulated as a chain reaction involving free radicals [2–4] or as a direct reaction between a carbanion and oxygen involving electron spin inversion in a radical pair intermediate.[5–8] Experimental support for both formulations has been supplied and in many instances it seems difficult to prove or disprove either of the two alternatives.

Phenols constitute substrates which are easily autoxidized in alkaline media due to the facile electron transfer from phenolate anions to oxygen. There exists a well-established correlation between the rate of autoxidation and the standard [9] or critical [10] redox potential in a series of mono-, di- and trivalent phenols. When dimeric products can be isolated, the autoxidation is usually interpreted as proceeding *via* phenoxy radicals.[10]

The autoxidation of phenols has been extensively studied using various types of substituted compounds and mild conditions.[10–14] The results of these studies have been explained in terms of reaction mechanisms involving the formation of cyclohexadienone hydroperoxides.[10–14] In a few favourable cases these intermediates have been isolated and their alkaline and thermal reactions have been investigated.[6,15,16] In general, the primary reactions of cyclohexadienone hydroperoxides can be classified as follows: (a) conversion to quinols,[17] (b) dehydration to quinones,[18] (c) rearrangement to epoxidated quinols [12,13,16] and (d) rearrangement with cleavage of the ring to muconic acid derivatives.[12,13]

The present work deals with the autoxidation of 4-*t*-butylguaiacol (*1*) in alkaline media. The reactions involved in the autoxidation of this compound should illustrate the behaviour of certain types of "uncondensed" phenolic units in lignins [19] and residual lignins under the conditions existing in oxidative-alkaline delignification processes.

RESULTS AND DISCUSSION

The autoxidation of 4-*t*-butylguaiacol (*1*) in alkaline (0.2 M NaOH) aqueous ethanol (EtOH:H_2O = 1:3) at 40 °C yielded a dimer *2*, an epoxide *3* and the acids *4*, *8* and *9* as main products (Scheme 1). The acid *4* was also obtained by autoxidation of epoxide *3* and the acids *8* and *9* by autoxidation of the *o*-quinone *6*. In addition the epoxide *3* yielded *5*, and the *o*-quinone *6* gave *10* and *11*. The pyrogallol derivative *7* gave only compound *8*. The experimental conditions used and the results

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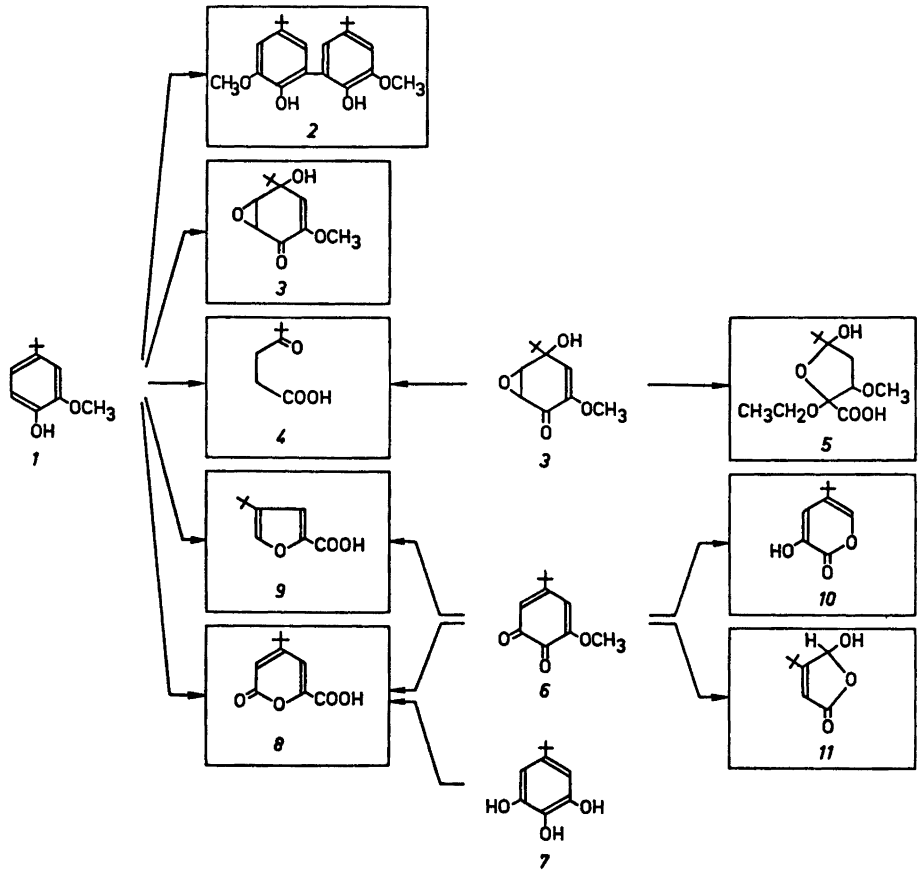
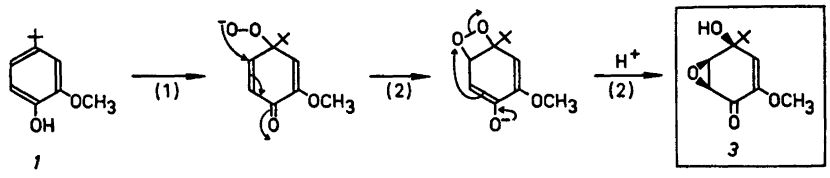


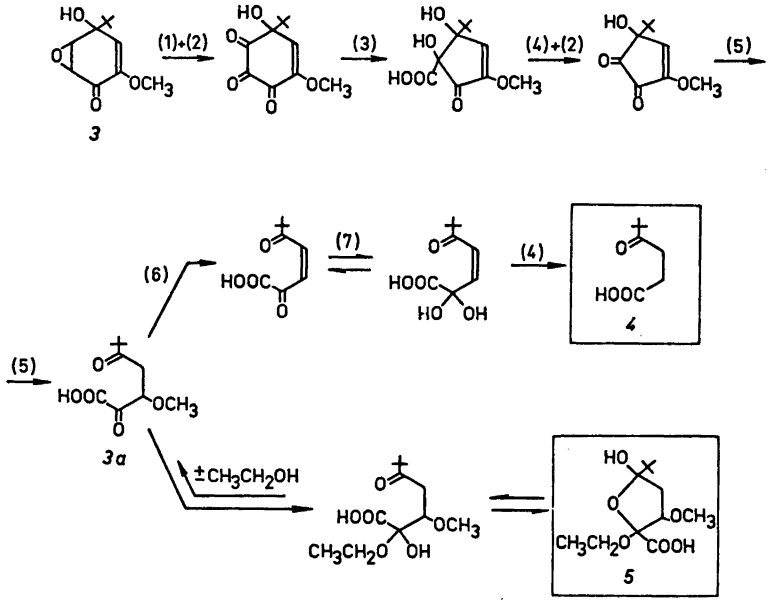
Scheme 1. Autoxidation of *1* and intermediates. (In this and the following Schemes, the products isolated are framed).

obtained are summarized in Table 1 (see EXPERIMENTAL).

Formation of 2. Compound *2*, a product of oxidative coupling, is also formed when *1* is treated in weakly alkaline solution with one-electron oxidants, such as potassium hexacyanoferrate(III).[20] It has moreover been shown [21] that other 4-alkyl substituted guaiacols react in the same way when exposed to similar conditions. The biphenyl structure of *2* exhibits remarkable stability toward oxygen in alkaline media. A possible explanation is that *2*, under the conditions used, exists as the monoanion in which the phenolic oxygens are protected against electron abstraction by intramolecular hydrogen bonding.[22,23] The monomethyl ether of *2* was oxidized at a rate comparable to that of compound *1*. This finding is in accordance



Scheme 2. Formation of *3* from *1*: (1) oxygenation,[6,13,15,16], (2) rearrangement.[13,16]



Scheme 3. Formation of *4* and *5* from *3*: (1) opening of epoxide ring, (2) enediol oxidation,[25,26] (3) benzilic acid rearrangement,[18,25–28] (4) decarboxylation of (vinylogous) β-keto acid,[25] (5) alkaline rearrangement,[15,26–28] (6) β-elimination, (7) hydration.

with the view that the degree of hydrogen bonding of the phenolate anion determines the oxidizability of the parent phenol.[22,23]

Formation of 3, 4 *and* 5. The reaction sequence leading to the formation of epoxide *3* is outlined in Scheme 2, in analogy to the mechanism proposed for the base-catalyzed autoxidation of other alkyl-substituted phenols.[13,16,24]

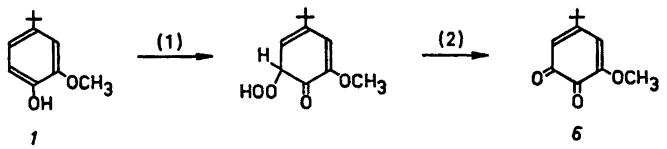
Compound *1* gave only a low yield of *3* under the reaction conditions used. In a separate experiment, using ethanol-water (1:1) as solvent, it was shown that this epoxide suffered alkaline-oxidative degradation. The main products were the γ-keto acid *4* and the α,δ-diketo acid *3a* isolated as its cyclic ethyl acetal *5* (Scheme 3). The formation of *4* from *3* indicates that the latter may be an intermediate in the alkaline-oxidative degradation of *1* (Scheme 1).

A plausible route for the formation of *4* and *5* from *3* is presented in Scheme 3. Analogous reactions found in the literature are referred to in the legend of the scheme.

The intermediacy of compound *3a* in the formation of *4* was supported by the isolation of the cyclic ethyl acetal *5*. The validity of Scheme 3 is further supported by the behaviour of 4,6-di-*t*-butylguaiacol during a similar oxidative-alkaline treatment.[24]

Formation of 6. The formation of the *o*-quinone *6* is outlined in Scheme 4. The route is analogous to that suggested for the formation of *p*-quinones upon autoxidation of phenols [16] and resorcinols [18] which are unsubstituted in the *para* position(s).

Formation of 8 – 11. When *6* was oxidized under the conditions given in Table 1, a rapid

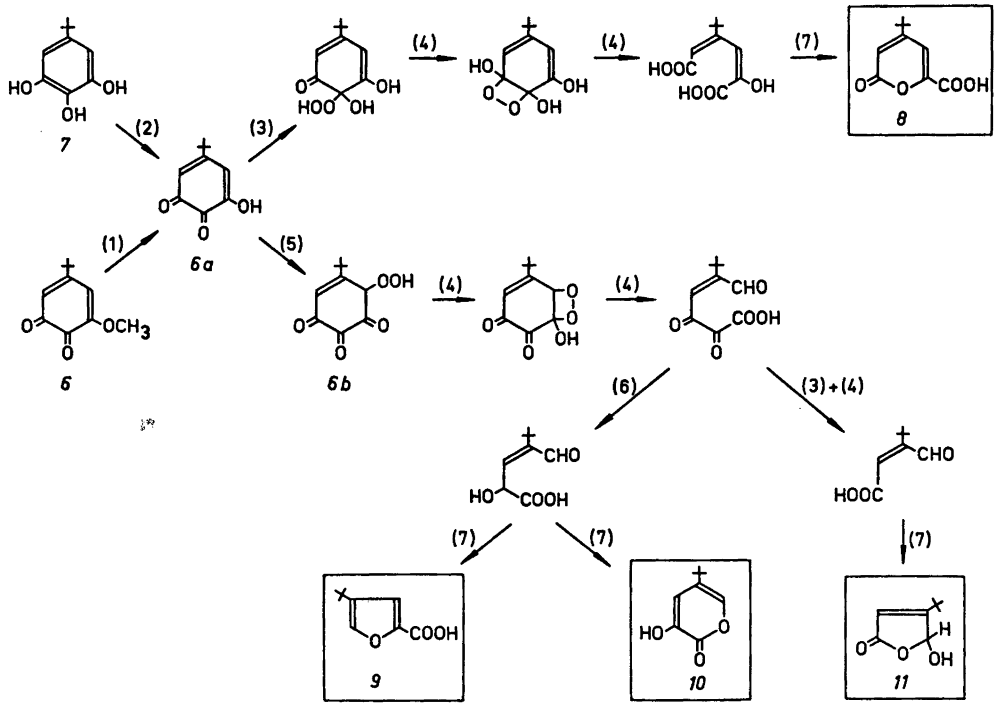


Scheme 4. Formation of *6* from *1*: (1) oxygenation,[29] (2) dehydration.[29]

Table 1. Alkaline autoxidation of model compounds at 40 °C in 0.2 – 0.3 M NaOH and with an oxygen consumption of 1 – 1.5 mol O_2/(mol model compound).

Compound (mol/l)	Solvent EtOH:H_2O [a]	Reaction time/h	Products (yielded % of theoretical)	Starting material recovered %
1 (0.1)	1:3	17	*2* (7), *3* (1.5), *4* (6), *8* (1), *9* (5), *12* [e] *13* [e]	35
2 (0.05)	6:1	48		90
2-Me ether (0.05)	6:1	20		60
3 (0.05)	1:1	11	*4* (12), *5* (15)	–
6 (0.05)	3:1	0.10	*8* (4), *9* (31), *10* (18), *11* (15)	–
7 (0.04)	1:1	0.15	*8* (85)	–
14 [b] (0.04)	1:3	20		*90* [c]
15 (0.05)	3:1	15		50 [d]

[a] The different ratios of EtOH:H_2O had to be used in order to ensure complete solubility of the compounds during the treatments. [b] Disodium salt of the *cis-trans*-forms. [c] Isolated as γ-lactone. [d] Determined by GC-analysis of the acidic fraction after methylation with diazomethane (reference: authentic compound). [e] Yield not determined.



Scheme 5. Formation of *8* – *11* from *6*: (1) alkaline demethoxylation, (2) enediol oxidation,[25,26] (3) hydrogen peroxide addition,[24] (4) rearrangements *via* dioxetanes,[31,32] (5) oxygenation, (6) decarboxylation of β-keto acid [25] after hydration, (7) cyclizations.

reaction took place and compounds *8*–*11* were formed. Compounds *8* and *9* were also isolated after autoxidation of *1* and it is therefore suggested that the *o*-quinone *6*, like the epoxide *3*, constitutes an intermediate in the alkaline-oxidative degradation of *1*. The remaining compounds (*10* and *11*) were not detected in the reaction mixture from *1*, probably due to further alkaline-oxidative conversions of these hydroxy lactones during the long period of treatment of *1* (Table 1). Thus, it has been shown[30] that 3-hydroxypyran-2-ones similar to compound *10* are converted into 2-furoic acids similar to *9* upon treatment with alkali.

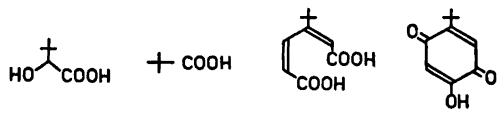
The proposed pathways of the oxidative-alkaline degradation of *6* are presented in Scheme 5.

The initial step of the reaction sequence (1) involves alkaline demethoxylation resulting in the formation of the hydroxy-*o*-quinone *6*a. Oxidation of *6*a by the action of hydrogen peroxide (3) gives ultimately *8* whereas oxygenation of *6*a (5) leads to *9*–*11*. The hydrogen peroxide required for step (3) may be generated by alkaline hydrolysis of *6*b to give the corresponding hydroxy triketone (*cf.* Refs. 9 and 17) and by subsequent autoxidation of the resulting dihydroxyquinone tautomers. A similar source of hydrogen peroxide should be the alkaline conversion of *6*a into the *vic*-tetrahydroxybenzene derivative followed by autoxidation of the latter. However, products expected to arise from *6*a and *6*b *via* such reactions have not been found so far in the autoxidation mixtures from *1* and *6*. During the autoxidation of 4-*t*-butylpyrogallol (*7*), hydrogen peroxide is produced in the first step (2) of the sequence and competes successfully with oxygen for the intermediate *6*a (3). Thus, a high yield of *8* is obtained (Table 1).

The pathways proposed for the formation of 8–11 (Scheme 5) also explain the formation of analogous products after similar oxidative treatments of 4,6-di-*t*-butylpyrogallol[33,34] and 4,6-di-*t*-butyl-3-ethoxy-*o*-quinone.[24]

An alternative to the route of carbon-carbon bond cleavage in Scheme 5 [step (4)] would involve addition of a hydroxide or alkoxide ion to the carbonyl adjacent to the hydroperoxy group, followed by rearrangement with heterolytic fission of the O–O bond without formation of dioxetanes (*cf.* Refs. 24 and 32).

The total yield of identified acidic and neutral products from *1* is low (Table 1). This may be partly due to further oxidation to simple aliphatic acids and carbon dioxide. Autoxidation of *1* and GC-MS analysis of the acidic fraction after esterification showed the presence of a great number of acidic degradation products. Compounds *12* and *13* were two of the main components in this fraction. Formic and acetic acids have not been taken into account in this study.



12 *13* *14* *15*

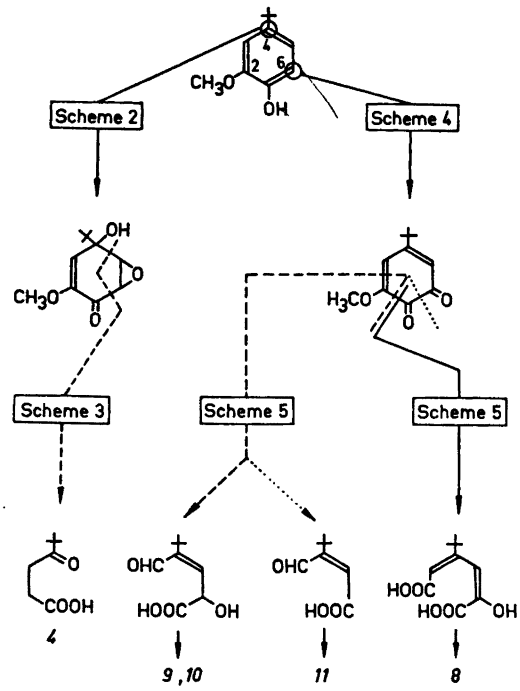
An alternative pathway starting with oxygenation of *1* in the 2-position (*cf.* behaviour of 4,6-di-*t*-butylguaiacol[24]) would lead to the muconic acid derivative *14* and/or to the hydroxyquinone *15*.[35] These oxidation products were, however, not found in the reaction mixture obtained from *1* although their stability under similar oxidative conditions was demonstrated in separate treatments of authentic compounds.

CONCLUSIONS

The *fragmentation* reactions of compound *1* are tentatively summarized in Scheme 6, in which the following steps are suggested.

The initial oxidative attack involves oxygenation preferentially in the 4- and 6-positions. Oxygenation in the *4-position* gives an epoxidated cyclohexadienone derivative (*3*, Scheme 2). This derivative undergoes alkaline and oxidative degradation (Scheme 3) resulting in the loss of the carbon atoms 5 and 6 by decarboxylations and of the methoxy substituent by β-elimination. The γ-keto acid *4* is the predominant product of this degradation route.

Oxygenation in the *6-position* affords an *o*-quinone (*6*, Scheme 4), which after alkaline demethoxylation undergoes two different oxidative conversions (Scheme 5). The first involves cleavage of the C^1-C^2 (or C^1-C^6) bond by hydrogen peroxide and leads to compound *8*. The second entails the cleavage of the orig-



Scheme 6. Fragmentations of *1*.

inal C^2-C^3 (or C^5-C^6) bond *via* oxygenation, followed by decarboxylation (loss of C^3 or C^6, formation of *9* and *10*) or by oxidative fragmentation (loss of C^1 and C^2 or C^1 and C^6, formation of *11*).

The oxidative degradation reactions of *1* compete with each other and with the oxidative coupling yielding the dimeric compound *2*. This product is more stable than the parent compound toward the standard treatment with oxygen-alkali. Thus, the oxidative coupling of *1* limits the extent of oxidative degradation.

EXPERIMENTAL

Materials

Synthesis of model compounds. The following compounds were prepared as previously described: *1*,[36] *2*,[37] *2*-monomethyl ether [20] and *7*.[38]

5,6-Epoxy-4-hydroxy-2-methoxy-4-t-butylcyclohex-2-enone (3). 4-*t*-Butylguaiacol (20 mmol) was treated with molecular oxygen in dimethylsulfoxide (200 ml) for 2 h using potassium *t*-butoxide (21 mmol) as base. After consumption of 1.2 equiv. of oxygen the mixture was neutralized with CO_2, diluted with water (500 ml) and extracted with chloroform (2 × 200 ml). The chloroform extract was washed with water, dried with sodium sulfate and evaporated. The residue (3.0 g) was purified by recrystallization from light petroleum (40 – 60 °C)-benzene (5:1) to give *3* as colourless crystals, yield 1.5 g (35 %). The compound was identical with the product isolated after alkaline autoxidation of *1* in ethanol-water (^{1}H NMR, MS, m.p.).

5-t-Butyl-3-methoxy-o-quinone (6). Sodium metaperiodate (0.05 mol) in water (250 ml) was added to a cooled (+ 5 °C) solution of 4-*t*-butyl-2,6-dimethoxyphenol [39] (0.05 mol) in 85 % acetic acid (600 ml). After 15 min, the reaction mixture was diluted with water and extracted with methylene chloride. The extract was washed with water, dried with sodium sulfate and evaporated to give 10 g of crude product. Crystallization from light petroleum gave *6* as dark-red crystals. Yield 3 g (30 %), m.p. 78 – 80 °C; Lit. 79 – 80 °C [40] and 86 – 88 °C.[20]

5-t-Butyl-2-hydroxy-p-quinone (15). 4-*t*-Butylcatechol (20 mmol) was treated with molecular oxygen [35] in an alkaline solution (0.3 M NaOH) containing ethanol-water (3:1) (200 ml) at 0 °C. After consumption of approximately 1.2 equiv. of oxygen (15 min), the reaction mixture was acidified (pH 1 – 2), diluted with water (300 ml) and extracted with chloroform. The chloroform extract was dried with sodium sulfate, filtered and evaporated to give 3.6 g of crude product. Recrystallization from toluene gave *15* as yellow crystals. Yield 1.7 g (51 %); m.p. 100 – 102 °C; Lit.[35] 101 – 103 °C. Methylation (CH_2N_2) of *15* gave the methyl ether. Yield 80 %; recrystallization from light petroleum, m.p. 162 – 164 °C; Lit.[20] 162 – 163 °C.

β-t-Butylmuconic acid (14). The method described for the preparation of β-methylmuconic acid [41] was adopted. Thus, 2-nitro-4-*t*-butylphenol [42] was treated with concentrated sulfuric acid at 110 °C yielding a γ-lactone (2,5-dihydro-5-oxo-3-*t*-butylfuran-2-acetic acid). Yield 22.5 %, m.p. 143 – 146 °C (benzene-light petroleum 2:1). Anal. $C_{10}H_{14}O_4$: C, H, O. ^{1}H NMR (60 MHz $CDCl_3$): δ 1.30 (s, 9 H, *t*-Bu), 3.07 (A), 2.57 (B), 5.42 (X), [CH_2 and CH; ABX; J_{AB} 16, J_{AX} 3 and J_{BX} 9 Hz], 5.90 (d, 1 H, ol, J 1.3 Hz, coupled to X). This lactone was converted to *14* (*cis-trans* form) as described for the corresponding methyl derivative.[41] *14* was characterized as the disodium salt. ^{1}H NMR (60 MHz, D_2O): δ 1.10 (s, 9 H, *t*-Bu), 5.90 (s, 1 H, ol), 6.08 (d, 1 H, ol, J 16 Hz), 7.28 (d, 1 H, ol, J 16 Hz).

Methods

Autoxidation of model compounds. The alkaline autoxidation of the model compounds was carried out in a three-necked 500 ml flask con-

nected to a gas burette. The quantity of oxygen consumed was measured. The reaction conditions and results are given in Table 1.

Work-up procedure. The reaction mixture was diluted with water, neutralized with carbon dioxide and extracted with ether to give the *neutral products.* The aqueous solution was then concentrated under reduced pressure (40 °C) to remove ethanol and acidified to pH 1 – 2 with hydrochloric acid or sulfuric acid. Subsequent extraction with ether afforded the *acidic products.*

The ether extracts were dried with sodium sulfate and evaporated under reduced pressure to give the crude reaction mixtures. The acidic products were methylated (in one instance ethylated) with diazomethane (diazoethane) prior to separation. Acetylation of several neutral compounds was performed with pyridine-acetic anhydride (1:1) (25 °C, 24 h).

Spectroscopy. The ^{1}H NMR spectra were obtained on a Perkin Elmer R-12 Spectrometer using deuteriochloroform ($CDCl_3$) as solvent.

The mass spectra were recorded on a Perkin Elmer 270 instrument at 25 eV using the direct inlet system or in combination with a gas chromatograph (Perkin Elmer 900).

The IR spectra were recorded on a Perkin Elmer 221 instrument and the UV and visible spectra on a Cary-118 C instrument.

Chromatography. Preparative separations were carried out by column chromatography using silica gel 60 (120 – 230 mesh ASTM, Merck) as adsorbant and mixtures of chloroform-ethyl acetate (19:1) or light petroleum (40 – 60 °C)-ethyl acetate in proportions from 9:1 to 7:3 as solvent systems. If necessary, the products were further purified by preparative thin-layer chromatography on silica gel H_{254} (Merck) using the same solvent systems as in column chromatography.

Gas chromatography. Analytical separations were carried out with a Perkin Elmer (F-30) gas chromatograph. The column material was OV-1 (10 %) on Chromosorb Q. In general, the temperature program, 100 – 200 °C, 4 °C/min, was used during a gas chromatographic run.

Product identification. MS, IR and UV data as well as m.p.'s and elemental analyses of the isolated products are given below. The analyses agree within ±0.3 % units with the calculated values unless otherwise stated. All mass fragments (max. 8) having $m/e > 100$ and intensities > 10 % of the base peak are listed.

3,3'-Dimethoxy-5,5'-di-t-butylbiphenyl-2,2'-diol (2), m.p. 166 – 168 °C. MS *m/e* (rel. int.): 358 (M, 80), 343 (M – 15, 95), 302 (M – 56, 20), 287 (M – 71, 100), 154 (25). IR (KBr): 3535 (m, OH), 1590 (m, aromatic). UV [MeOH (ε)]: 284 (7050).

5,6-Epoxy-4-hydroxy-2-methoxy-4-t-butylcyclohex-2-enone (3), m.p. 100 – 102 °C. Anal. $C_{11}H_{16}O_4$: C, H, O. MS *m/e* (rel. int.): 156 (M – 56, 75), 155 (M – 57, 70), 141 (M – 71, 65), 138 (M – 74, 30), 137 (70), 113 (100), IR (KBr): 3480 (s, OH), 1690 (s, C=O), 1625 (m, C=C–C=O). UV [MeOH (ε)]: 273 (4540).

Methyl 5,5-dimethyl-4-oxo-hexanoate (methyl ester of 4), amorphous. Anal. $C_9H_{16}O_3$: C, H, O. MS *m/e* (rel. int.): 141 (M – 31, 10), 115 (M – 57, 100), 113 (M – 59, 10), 87 (M – 85, 10). IR ($CHCl_3$): 1730 (s, C=O), 1700 (s, C=O).

Methyl tetrahydro-5-t-butyl-2-ethoxy-5-hydroxy-3-methoxy-2-furoate (methyl ester of 5), amorphous. (Found: C 58.16; H 8.44; O 33.33. Calc. for $C_{13}H_{24}O_6$: C 57.39; H 7.82; O 34.78). MS *m/e* (rel. int.): 230 (M – 46, 16), 212 (M – 64, 14), 169 (M – 107, 30), 167 (M – 109, 20), 157 (15), 129 (25), 127 (85), 115 (100). IR ($CHCl_3$): 3420 (m, OH), 1740 (s, C=O).

4-t-Butyl-6-methoxycarbonyl-(2H)-pyran-2-one (methyl ester of 8), m.p. 84 – 86°C. Anal. $C_{11}H_{14}O_4$: C, H, O. MS *m/e* (rel. int.): 210 (M, 25), 182 (M – 28, 10), 167 (M – 43, 15), 151 (M – 57, 100). IR (KBr): 1730 (s, C=O), 1715 (s, C=O), 1640 (w, C=C–C=O) 1545 (s, C=C–C=O). UV [MeOH (ε)]: 298 (7000).

Methyl 4-t-butyl-2-furoate (methyl ester of 9), amorphous. Anal. $C_{10}H_{14}O_3$: C, H, O. MS *m/e* (rel. int.): 182 (M, 15), 167 (M – 15, 100), 151 (M – 31, 10), 139 (M – 43, 12). IR ($CHCl_3$): 1710 (s, C=O), 1590 (s, C=C), 1505 (m, C=C). UV [MeOH (ε)]: 263 (–).

3-Acetoxy-5-t-butyl-(2H)-pyran-2-one (acetate of 10), m.p. 97 – 99 °C. Anal. $C_{11}H_{14}O_4$: C, H, O. MS *m/e* (rel. int.): 168 (M – 42, 70), 153 (M – 57, 80), 140 (M – 70, 15), 125 (M – 85, 100). IR (KBr): 1760 (m, C=O). 1710 (s, C=O), 1635 (m, C=C–C=O), 1545 (m, C=C–C=O). UV [MeOH (ε)]: 295 (6520).

γ-Acetoxy-β-t-butyl-$\Delta^{\alpha,\beta}$-butenolide (acetate of 11), amorphous. (Found: C 61.33; H 7.07; O 31.68. Calc. for $C_{10}H_{14}O_4$: C 60.60; H 7.07; O 32.32). MS *m/e* (rel. int.): 156 (M – 42, 12), 141 (M – 57, 17), 139 (M – 59, 30), 138 (M – 60, 38), 111 (50), 110 (90), 95 (100). IR ($CHCl_3$): 1765 (s, C=O), 1630 (m, C=C–C=O).

^{1}H NMR data are presented in Table 2.

The presence of the low molecular weight acids *12* (3,3-dimethyl-2-hydroxybutyric acid) and *13* (2,2-dimethylpropionic acid) in the reaction mixture obtained on autoxidation of *1* was shown by GC-MS analyses of the ethyl esters (ethylation with diazoethane) and in case of *12* also as the acetate of the methyl ester.

Ethyl ester of 12. MS *m/e* (rel. int.): 104 (M – 56, 55), 87 (M – 73, 40), 75 (56), 69 (70), 57 (100).

Methyl ester of 12 *(acetate).* MS *m/e* (rel. int.): 157 (M – 31, 5), 132 (M – 56, 40), 129 (M – 59, 25), 90 (100), 87 (55), 69 (20), 67 (30), 57 (60).

Ethyl ester of 13. MS *m/e* (rel. int.): 130 (M, 5), 115 (M – 15, 3), 87 (M – 43, 10), 57 (100).

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Table 2. ^{1}H NMR of products isolated from alkaline autoxidation of *1*, *3*, *6*, and *7*. 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	1.31 [a]	3.90 [b] (et)	6.91 (s, 4 H, ar), 5.98 (s, 2 H, OH)
3	1.03	3.59 (et)	2.42 (broad s, 1 H, OH), 3.75 (A), 3.51 (B), 5.29 (X) [ol, CH, CH; ABX; J_{AB} 4.7, J_{AX} 2.7, $J_{BX}\sim 0$ Hz]
4 [c]	1.16	3.63 (es)	2.59 (A) and 2.79 (B) [CH_2 and CH_2; A_2B_2; J_{AB} 6.4 Hz]
5 [c]	0.94	3.73 (es)	2.36 (broad s, 1 H, OH); 2.26 (A), 2.02 (B) and 3.96 (X) [CH_2 and CH; ABX; J_{AB} 14.3, $J_{AX}\sim 6$, $J_{BX}\sim 9$ Hz], 3.61 (q, 2 H, CH_2), 1.03 (t, 3 H, CH_3), J_{CH_2,CH_3} 7.3 Hz
8 [c]	1.25	3.90 (es)	6.36 (d, 1 H, ol), 7.13 (d, 1 H, ol), $J_{ol,ol}$ 1.7 Hz
9 [c]	1.23	3.85 (es)	7.10 (d, 1 H, ol), 7.28 (d, 1 H, ol), $J_{ol,ol}$ 0.6 Hz
10 [d]	1.21	2.29 (ac)	7.21 (s, 2 H, ol)
11 [d]	1.21	2.13 (ac)	5.90 (d, 1 H, CH), 7.0 (d, 1 H, ol), $J_{ol,CH}$ 0.8 Hz

[a] 18 H. [b] 6 H. [c] Methyl ester. [d] Acetate.

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