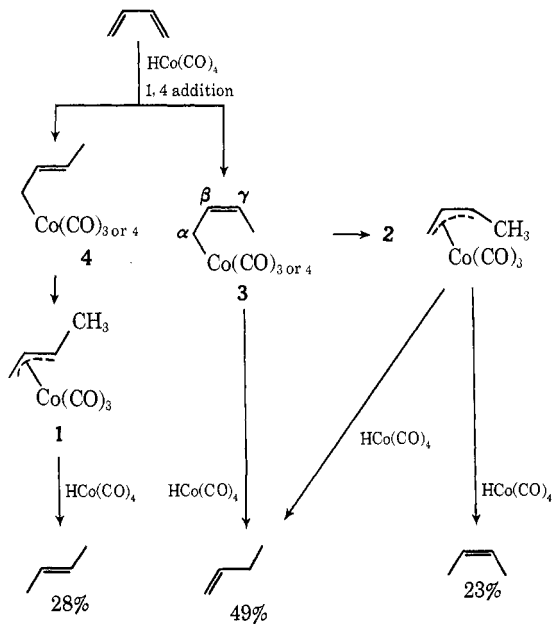
CHART I
A SCHEME FOR THE HYDROGENATION OF BUTADIENE WITH $HCo(CO)_4$



49% 1-butene, 23% *cis*-2-butene, and 28% *trans*-2-butene. Although we have shown that the π-allyl complexes **1** and **2** are both directly converted to butenes, the distribution of products from the butadiene reaction cannot be explained by the intermediacy of only these two complexes; another complex leading directly to 1-butene is required. This may very well be the σ complex **3** (Chart I), a precursor to **2**. The various reactions of importance which best explain the results are shown in Chart I. We believe that hydride attack at the γ carbon atom of intermediate **3**, accompanied by bond migration and elimination of cobalt, produces 1-butene almost exclusively. An analogous reaction with the complex **4** probably is repressed by steric factors, and hence **4** is rapidly converted to **1**, which yields *trans*-2-butene almost exclusively. Because attack of $HCo(CO)_4$ on **1** provides little 1-butene, it is also reasonable to assume that such attack on **4** is similarly ineffective in giving 1-butene while **3** is much more exposed to a γ attack. Analogous explanations have been used to explain product distribution from butadiene in the $[Co(CN)_5H]^{3-}$ system.[18] A σ complex arising from 1,2 Markovnikov addition is also a possible intermediate leading to 1-butene.

Although Chart I outlines what we consider to be the principal reactions, it must be kept in mind that equilibria probably exist between many of the species and that the number of coordinated carbon monoxides is variable.

Registry No.—**1**, 31627-44-8; **2**, 31627-45-9; butadiene, 106-99-0; cobalt hydrocarbonyl, 17186-02-6; 1-pentene, 109-67-1.

Acknowledgment.—The authors are grateful to the donors to the Petroleum Research Fund administered by the American Chemical Society for the support which made this work possible.

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Peroxyacetic Acid Oxidation of 4-Methylphenols and Their Methyl Ethers[1]

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The peroxyacetic acid oxidations of 4-methylpyrocatechol, 4-methylveratrole, *p*-cresol, *p*-methylanisole, 2-methoxy-*p*-cresol, and 4-methyl-*o*-benzoquinone were investigated in aqueous acetic acid at 25°. In all cases, *cis,trans*-β-methylmuconic acid and the related lactones γ-carboxymethyl-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone and γ-carboxymethyl-γ-methyl-$\Delta^{\alpha,\beta}$-butyrolactone were produced. With the exception of 4-methyl-*o*-benzoquinone, the substrates all produced γ-carboxymethyl-γ-hydroxy-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone. This product was suggested to arise from electrophilic hydroxylation ortho to the methyl substituent and para to an oxygen-bearing substituent followed by aromatic ring cleavage and lactonization. Similar hydroxylation was evident in the formation of 4-hydroxy-4-methyl-2,5-cyclohexadienone from *p*-cresol and *p*-methylanisole. 4-Methylveratrole and *p*-methylanisole each gave 2-methoxy-5-methyl-*p*-benzoquinone as a major product. This product was slowly oxidized in the presence of excess peroxyacetic acid. Although the combined yields of identified products were low, stoichiometry data on oxidant and substrate consumption for the unmethylated compounds agreed with that predicted on the basis of the products formed. Higher than predicted ratios of oxidant consumed/substrate consumed were found for the methylated substrates. The results can be accounted for on the basis of competitive pathways involving hydroxylation at activated ring positions, demethoxylation, ortho and para quinone formation, and aromatic ring cleavage.

Hydroxylation appears to be an important result of reactions between peroxy acids and many aromatic compounds. Thus, oxidation of *m*-xylene by trifluoroperoxyacetic acid gave 2,4- and 2,6-xylenol along with the corresponding *p*-quinone.[2] Oxidation of phenol by peroxyacetic acid is known to produce *p*-benzoquinone and muconic acid;[3-5] apparently, initial para and ortho hydroxylation are followed by further oxidation to the para quinone and the muconic acid, respectively. Peroxyacetic acid was reported to convert *p*-cresol to *cis,trans*-β-methylmuconic acid and a related lactone.[3,6] The muconic acid derivatives have also been reported

(1) A portion of a thesis submitted by J. C. Farrand in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis., June 1969.

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TABLE I
PRODUCT YIELDS

Substrate	Reaction, %	Reaction time, hr	Product yield, % of theoretical: Muconic acids[a]	γ-Hydroxy lactone	p-Quinone	Dienone	2-Hydroxy-p-methylanisole	Total[a]
I	100	2–40	42 (56)	5				47 (61)
II	84	30	9 (13)	1	17			27 (31)
III	72	60	23 (32)	4		12		39 (48)
IV	25	40	8 (12)	2		22	6	38 (42)
IV	45	72	8 (15)	2	16	16	2	44 (51)
V	85	24	11 (20)	13				24 (33)
XI	100	0.1	70 (70)					70 (70)
XI	100	26	41 (55)					41 (55)

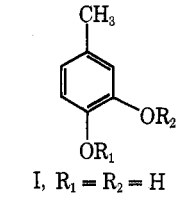
[a] The yield given in parentheses includes the identified acids and unidentified components believed to be isomeric acids; their amounts were approximated by the glc analysis.

as products from similar oxidations of pyrocatechol and 4-methylpyrocatechol.[4,6,7]

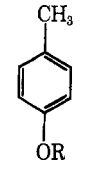
Somewhat similar findings have been reported for phenyl ethers. *p*-Quinones have been observed as products, although yields were low and water-soluble reaction products were not investigated.[8,9] Oxidation of 4-methylveratrole with peroxyacetic acid has been shown to give 2-methoxy-5-methyl-*p*-benzoquinone, which clearly involves demethylation.[9] Few well-defined examples of ring cleavage (muconic acid formation) induced by peroxy acid oxidation of phenyl ethers exist. Peroxybenzoic acid oxidized veratrole to dimethyl muconate[8] in 1% yield; naphthyl and phenanthryl methyl ethers underwent cleavage of the oxygenated ring,[10,11] producing carboxylic acids.

From investigations of peroxy acid oxidations of phenolic systems which have been carried out thus far, it is clear that these reactions are complex. *p*-Quinone and muconic acid formation have been observed, but the yields have generally been low. A clearer understanding of the course of such oxidations should ultimately lead to a better understanding of a much more complex situation, namely, oxidative delignification of wood. Peroxyacetic acid is known[12–16] to react with and solubilize the lignin (which contains phenolic and phenyl ether moieties) of certain wood species. It is clear that the oxidation can be quite selective in that very little carbohydrate material is oxidized; this is in marked contrast to conventional sulfur-based pulping procedures where dissolution of comparable amounts of lignin and carbohydrate occur. Evidence has been found that ring cleavage and demethylation do occur in peroxyacetic acid delignification.[17–20]

This study focused primarily on identification of reaction products, estimation of their amounts, and reaction stoichiometry in the peroxyacetic acid oxidations of 4-methylpyrocatechol (I), 4-methylveratrole (II), *p*-cresol (III), and *p*-methylanisole (IV). In addition, it was possible to obtain evidence for the existence of certain intermediates. All oxidations were carried out with a 3:1 mole ratio of oxidant to substrate in 10% peroxyacetic acid in aqueous acetic acid (17% by water weight) at room temperature. Reaction times depended on substrate reactivity and ranged from a few minutes to several days.



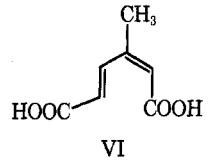
I, $R_1 = R_2 = H$
II, $R_1 = R_2 = CH_3$
V, $R_1 = H$; $R_2 = CH_3$
XIV, $R_1 = CH_3$; $R_2 = H$



III, R = H
IV, R = CH_3

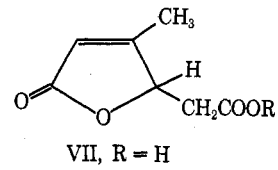
Results and Discussion

Table I includes the oxidation products formed and their yields. The common feature of all of the oxidadations studied is the finding of "muconic acids." This term includes *cis,trans*-β-methylmuconic acid (VI) and the two five-membered-ring lactones (VII and VIII) isomeric with VI. Aromatic ring cleavage, therefore, is an important mode of reaction regardless of whether there is initially one oxygen on the ring or two. Methoxyl groups clearly do not prevent ring cleavage,



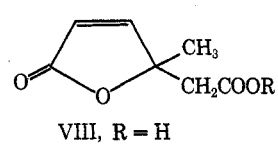
VI

+



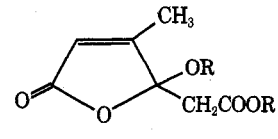
VII, R = H
VII–E, R = CH_3

I ⟶



VIII, R = H
VIII–E, R = CH_3

+



IX, R = H
IX–E, R = CH_3

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(8) S. L. Friess, A. H. Soloway, B. K. Morse, and W. C. Ingersoll, *J. Amer. Chem. Soc.*, **74**, 1305 (1952).
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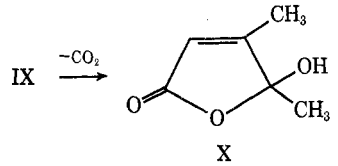
although *p*-quinone formation is competitive in these cases.

In the oxidation of 4-methylpyrocatechol, the dominant result is ring cleavage giving VI, along with related lactones γ-carboxymethyl-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (VII) and γ-carboxymethyl-γ-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (VIII).

Formation of VIII cannot result from VI because of the latter's cis,trans stereochemistry. Undoubtedly, the relatively unstable[6] *cis,cis*-β-methylmuconic acid is formed initially and is isomerized partly to the cis,trans acid and partly to VIII as well as other isomers (see Table I, footnote *a*). Earlier work[6] has shown both VI and VII to be formed, but the γ-methyl lactone (VIII) was not previously reported. The structural assignment is strongly supported by nmr and mass spectral data of the monomethyl ester (VIII-E). The doublets (J = 5.5 Hz) at δ 6.03 and 7.65 support cis vinyl protons, since known $\Delta^{\alpha,\beta}$-butyrolactone gives virtually the same chemical shifts for its vinyl protons. The $-CH_2-$ group appears as an AB pattern in contrast to the ABX pattern so clearly revealed in VII-E; the δ values are 2.70 and 2.92 for VIII-E and 2.63 and 2.84 for VII-E. The mass spectrum verified the molecular weight of VIII-E and also showed the fragmentation expected from such a structure. The base peak at m/e 97 must arise from loss of $-CH_2COOCH_3$ from the parent ion (m/e 170). A similar loss of the side chain was observed in the mass spectrum of VII-E and, indeed, this is common for lactones.[21,22]

The other product of 4-methylpyrocatechol oxidation found in this study was γ-carboxymethyl-γ-hydroxy-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (IX). This product gave a dimethyl derivative IX-E, which gave nmr and mass spectra strongly supporting the assigned structure. The β-methyl group and the α-vinyl proton showed, as expected, signals very similar to the corresponding β-methyl lactone (VII-E) signals. The $-CH_2-$ group appeared as an AB pattern rather than an ABX as in VII-E. Again, the base peak at m/e 127 in the mass spectrum of IX-E was indicative of loss of a $-CH_2COOCH_3$ side chain from the parent ion (m/e 200). Loss of $-OCH_3$ was also suggested by a peak at m/e 169. It was discovered that IX readily decarboxylates on the gas chromatograph giving β,γ-dimethyl-γ-hydroxy-$\Delta^{\alpha,\beta}$-butyrolactone (X). The nmr spectrum strongly supports this structure assignment.



X

The stoichiometry (moles of peroxy acid consumed/moles of substrate consumed) results are shown in Table II. Also shown are predicted stoichometries which were derived on the basis of the structures and amounts of the products formed. The agreement between predicted and experimental stoichiometries in the 4-methylpyrocatechol oxidation was excellent. Since the γ-hydroxy lactone (IX) required 3 mol of oxidant per 1 mol of the catechol (I), a slight excess consumption of oxidant above 2.0 was expected.

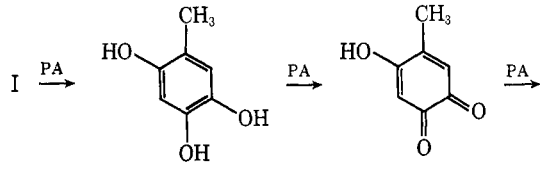
TABLE II
OXIDATION STOICHIOMETRY

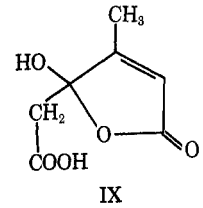
Substrate	Reaction, %	Stoichiometry[a] Exptl	Predicted
I	100	2.1	2.1
II	18	2.2	
II	80	2.9	2.0
III	40	2.8	
III	60	2.8	2.6
IV	8	1.7	
IV	45	3.0	2.3
V	85	3.0	2.4
XI	100	1.0	1.0

[a] Moles of oxidant consumed/moles of substrate consumed.

Further insight into the course of the oxidation of I was sought through an oxidation of 4-methyl-*o*-benzoquinone (XI). Since *o*-quinones have been implicated by others[4,23-27] as precursors to muconic acids in a variety of systems, it seemed reasonable that XI was an intermediate here in the formation of β-methylmuconic acid (VI) and the isomeric lactones (VII, VIII). This view was supported by the fact that peroxyacetic acid oxidation of XI gave VI, VII, and VIII in essentially the same distribution observed in the oxidation of I. In addition, at least three unknown acids are also formed in the same relative amounts from both I and XI. It is also noteworthy that the γ-hydroxy lactone (IX) was not produced from the *o*-quinone (XI).

From the above, it would appear that there are two competitive oxidation pathways involved in the 4-methylpyrocatechol oxidation: (1) conversion to the *o*-quinone XI followed by oxidation to the muconic acid products (VI, VII, and VIII); and (2) hydroxylation (effectively electrophilic attack of OH^+ donated by PA)[28] at the 5 position of 4-methylpyrocatechol followed by ring cleavage and lactonization to IX as shown below. It can further be argued that such ring hydrox-





IX

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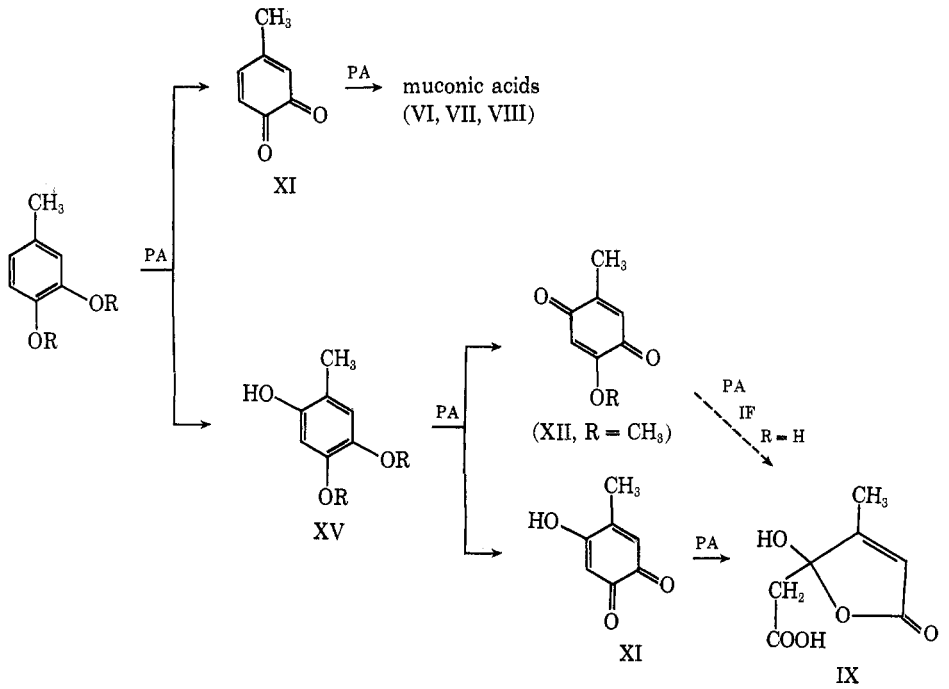
(28) Evidence that peroxy acid hydroxylation is the result of electrophilic attack by OH^+ (although OH^+ is probably not a discreet intermediate) and not the hydroxyl radical has been summarized by Norman and Smith.[27] We found no evidence for a free-radical process in experiments where methyl methacrylate was added to the oxidation system.

ylation should be more competitive if *o*-quinone formation is hampered by the need for prior demethylation. A test case was 2-methoxy-*p*-cresol (V). Here, indeed, the yield (Table I) of the γ-hydroxy lactone was more than twice that found in the catechol oxidation. Demethylation did occur, and the usual distribution of muconic acids (VI, VII, VIII) was observed.

In agreement with earlier work[9] 4-methylveratrole (II) was found to give 2-methoxy-5-methyl-*p*-benzoquinone (XII) as a major product of peroxyacetic acid oxidation. However, the present work has further shown that ring cleavage to muconic acids also occurs and that a small amount (1%) of the γ-hydroxy lactone (IX) is produced. The overall yield of products (Table I) was quite low, and this was reflected in the observed stoichiometry (Table II), which showed a substantially higher oxidant consumption than was predicted. The stoichiometry was found to increase as the reaction of 4-methylveratrole proceeded. This finding prompted a study of the stability of the known reaction products to further oxidation. Neither the muconic acid (VI) nor the β-methyl lactone (VII) consumed any significant amount of peroxyacetic acid in control experiments. The *p*-quinone (XII) was shown to be slowly oxidized, consuming 1.0 mol of oxidant per 1 mol of XII; product analysis was unsuccessful. It is doubtful that the increasing stoichiometry in the oxidation of 4-methylveratrole can be entirely accounted for by further oxidation of the *p*-quinone because the rate of that secondary oxidation would appear to be too slow.

The results of the 4-methylveratrole study show considerable similarity to the other dioxygenated substrates (I, XI, V). The following scheme emphasizes the previously discussed competitive pathways involving *o*-quinone formation and C-5 hydroxylation of the ring.



This latter pathway can lead either to the *p*-quinone (XII) or to the γ-hydroxy lactone (IX) depending on the retention of the C-1 methoxyl group. The mechanism of demethylation is not known, but may well involve displacement of methoxy by hydroxyl *via* a hemiacetal intermediate. Although methoxyl groups do not appear to substantially alter the reaction pathways involved, they do retard the oxidation rate considerably (Table III). 4-Methylpyrocatechol is consumed about 20 times faster than either 4-methylveratrole (II) or 2-methoxy-*p*-cresol (V).

TABLE III

RELATIVE REACTIVITY OF SUBSTRATES[a]

Substrate	Half-life, hr[b]	Substrate	Half-life, hr[b]
4-Methyl-*O*-benzoquinone (XI)	0.01	4-Methylveratrole (II)	5
4-Methylpyrocatechol (I)	0.2	*p*-Cresol (III)	25
2-Methoxy-*p*-cresol (V)	4.0	*p*-Methylanisole (IV)	100

[a] Conditions: 10% peroxyacetic acid, 3:1 mole ratio favoring oxidant, 25°. [b] Time required for disappearance of 50% of substrate.

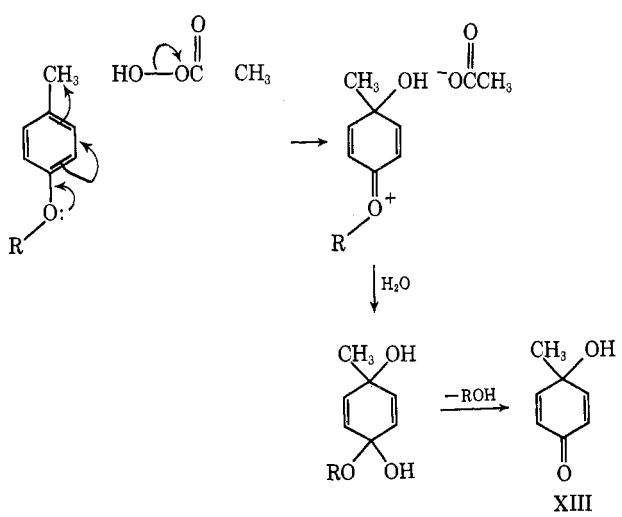
The above proposed reaction pathways place considerable emphasis on hydroxylation of the initial reactant to give an intermediate (XV). This proposed intermediate has not been studied independently or isolated during the reaction (it is probably too reactive); it is inferred as a reasonable hypothesis on the basis of the products. Further support that ring hydroxylation can occur in the oxidant system was obtained by showing that mesitylene (1,3,5-trimethylbenzene) was oxidized to hydroxymesitylene along with other products. More directly, evidence was obtained that 2-hydroxy-*p*-methylanisole (XIV) was an intermediate in the oxidation of *p*-methylanisole (IV) (discussed in greater detail below).

The oxidations of *p*-cresol (III) and *p*-methylanisole (IV) are very similar to the oxidations described above in the sense that ring cleavage to muconic acids is important (Table I). The *p*-quinone (XII) results from IV as it did from II. Hydroxylation ortho to the oxygen-containing substituent can provide a precursor for *o*-quinone formation and, ultimately, muconic acid systems. In the case of IV, this was clearly seen by our ability to detect 2-hydroxy-*p*-methylanisole (XIV) as a

product. In numerous experiments, its yield was always lower (2 *vs.* 6%) at 45–55% reaction (of IV) than at 25% reaction. Thus, it is considered as a probable intermediate in the formation of muconic acids, *p*-quinone (XII), and γ-hydroxy lactone (IX). Similarly, 4-methylpyrocatechol (I) may well be one of the intermediates in the oxidation of *p*-cresol (III) although its reaction rate would be much too great to permit identification. This idea is supported by the finding that catechol is a probable intermediate in the peroxyacetic acid oxidation of phenol.[27]

Along with ortho hydroxylation in these substrates bearing a single oxygen, it is also clear that para hydroxylation occurs. Both III and IV gave 4-hydroxy-4-methyl-2,5-cyclohexadienone (XIII) in relatively large amounts. This compound has been previously reported as a product of aqueous hydrogen peroxide oxidation of *p*-cresol.[29] (It is not believed that hydrogen peroxide is an active oxidant under the conditions of this study because its concentration was kept below 0.3%.) The assignment of structure XIII was supported by ir, nmr, and mass spectra. The infrared spectrum agrees very well with spectra previously reported for cyclohexadienones.[30] The plane of symmetry in the molecule is clearly evident from the pair of doublets (J = 10 Hz) for the vinyl protons at δ 6.13 and δ 6.95 which each contain *two* identical protons; in addition, the methyl group appears as a singlet at δ 1.48. The mass spectrum gives a base peak (*m/e* 109) corresponding to loss of $-CH_3$. The peaks at *m/e* 81 and 96 may both arise by loss of carbon monoxide from the *m/e* 109 ion and the parent ion (*m/e* 124), respectively. In the latter case, the molecular ion probably undergoes ring opening with methyl migration to the adjacent carbon (a fairly common event in similar systems)[31] prior to elimination of CO.

The dienone can be visualized to form from either *p*-cresol or *p*-methylanisole as shown (where R = H or CH_3). The peroxyacetic acid acts as a donor of OH^+



XIII

to an aromatic nucleus activated for electrophilic attack. Subsequent reaction of the intermediate with water can then lead to demethoxylation of *p*-methylanisole.

The stoichiometry results from *p*-cresol oxidation are in reasonable agreement with the results predicted. This is not the case for *p*-methylanisole. In fact, all three methylated substrates (II, IV, and V) brought about higher oxidant consumption than could be predicted on the basis of identified products. Time dependence of stoichiometry was observed for the methylated substrates II and IV, but it was not observed for the unmethylated reactants (I and III). In view of the low yields of identified products, it is difficult to explain this difference. Further oxidation of the *p*-quinone (XII) which is formed only from II and IV, may be partly responsible, but, as was pointed out above, the rate of oxidation of XII does not appear great enough to account entirely for the experimental stoichiometries. Thus, some other unknown oxidative process probably contributes with the methylated systems. In the case of unmethylated systems where experimental stoichiometries agree with calculated values, the products unaccounted for may well arise from side reactions of intermediates and reaction products with each other. Some possibilities would include Diels–Alder reactions of quinones and possibly a reaction of the intermediate *o*-quinone with 4-methylpyrocatechol in a manner somewhat analogous to reaction of catechol with *o*-benzoquinone.[27]

Control experiments showed that 80–85% of the β-methyl lactone (VII) could be recovered after being subjected to the entire work-up procedure. However, only 47% of *cis,trans*-β-methylmuconic acid could be recovered (in the form of β-methyl lactone VII) when subjected to the work-up procedure.

Experimental Section

Analytical Methods.—Infrared spectra were determined using either a Perkin-Elmer Model 21 (prism) or a Model 621 grating spectrophotometer. A beam condenser was used for microsamples. A Varian Associates A-60A spectrometer equipped with a spin decoupler was used for the nmr spectra; tetramethylsilane and sodium 2,2-dimethyl-2-silapentane-5-sulfonate were used as internal standards in deuteriochloroform or deuterium oxide, respectively. Small quantities were analyzed using a semimicro sample tube (125 μl). Complex signals such as ABX patterns were analyzed by the procedure described by Garbisch.[32] Mass spectra were determined by Morgan–Schaffer Corp., Montreal, Canada using a Hitachi RMU-6D mass spectrometer. Low voltage spectra allowed confirmation of suspected parent ion peaks. Intensities were approximated by measuring peak heights.

A Varian Aerograph Moduline 202-C dual column gas chromatograph with a linear temperature programmer and thermal conductivity detector was used for glc. The following glc columns were employed: column A was a 5 ft × 0.25 in. o.d. stainless steel tube, packed with 15% Carbowax 20M on 60/80 mesh Chromosorb W (DMCS treated, acid washed); column B was a 5 ft × 0.25 in. o.d. stainless steel tube packed with 20% SE-30 on 60/80 Chromosorb W (DMCS treated, acid washed); column C was a 6 ft × 0.375 in. o.d. stainless steel tube packed with 15% Carbowax 20M on Chromosorb W (DMCS treated, acid washed).

Column A was used for separation of reactants, volatile reaction products, and methyl ester derivatives of carboxylic acids. Column B was used for analysis of 2-methoxy-5-methyl-*p*-benzoquinone (125°, 75 ml/min He) and all silylated carboxylic acids (165°, 75 ml/min). Column C was used for collecting oxidation products. Internal standards were selected for quantitative analyses, and response factors were measured; peak areas were determined by a Technicon Model AAG integrator/calculator.

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Chemicals.—Most of the compounds were purchased including *p*-methylanisole, *p*-cresol, 4-methylpyrocatechol, 4-methylveratrole (all from K & K Laboratories, Inc.), mesitylene (Aldrich Chemical Co.), and 2-methoxy-*p*-cresol (Eastman Organic Chemicals). These were all checked for purity by glc and were used without further purification.

4-Methyl-*o*-benzoquinone was prepared by oxidation of 4-methylpyrocatechol with tetrachloro-*o*-benzoquinone.[33] The product was washed with dry ether and stored over phosphorus pentoxide. The structure was confirmed by infrared and nmr analysis.

γ-Carboxymethyl-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (VII) was prepared by reaction of concentrated sulfuric acid with 2-nitro-*p*-cresol.[34] The extracted product was recrystallized twice from water and once from ethanol–benzene (1:3) giving colorless crystals: mp 126.2–128.0° corrected (lit.[34] mp 130°); ir (KBr) 2580 (broad, carboxyl OH), 1730 (vs), 1687 (vs, C=O), 1640 cm^{-1} (m, C=C); nmr (D_2O) δ 2.04 (doublet of doublets, 3 H, J = 1.5, 0.8 Hz, β-CH_3), 2.68 (doublet of doublets, 1 H, J = 16.5, 8.4 HCH in an ABX pattern), 3.13 (doublet of doublets, 1 H, J = 16.5, 3.6 Hz, HCH in an ABX pattern), 5.43 (multiplet, 1 H, J = 8.4, 3.6, 0.8 Hz, γ H in an ABX pattern), and 6.00 ppm (quintet, 1 H, J = 1.5 Hz, α-vinyl H).

Methylation of the acid with 5% methanolic HCl followed by preparative glc on column C gave the methyl ester of γ-carboxymethyl-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (VII-E) as an oil: ir (neat) 1760 (vs), 1740 (vs, broad, C=O), 1642 cm^{-1} (m, C=C); nmr ($CDCl_3$) δ 2.10 (multiplet, 3 H, β-CH_3), 2.63 (doublet of doublets, 1 H, J = 16.5, 7.7 Hz, HCH in an ABX pattern), 2.84 (doublet of doublets, 1 H, J = 16.5, 4.3 Hz, HCH in an ABX pattern), 3.77 (s, 3 H, ester CH_3), 5.25 (m, 1 H, γ H in an ABX pattern), and 5.86 ppm (m, 1 H, α-vinyl H); mass spectrum (70 eV) *m/e* (rel intensity) parent ion 170 (20), 139 (14), 111 (30), 110 (78), 97 (93), 69 (100), 68 (38).

Peroxyacetic acid was prepared by the hydrogen peroxide oxidation of acetic acid with sulfuric acid catalyst.[35] The reaction mixture was distilled giving a final solution containing approximately 35% peroxyacetic acid, 0.1% hydrogen peroxide, 5% acetic acid, and 60% water. This solution was stored at 5°. All glassware that came in contact with peroxyacetic acid was first passivated by soaking with detergent, sodium hydroxide, nitric acid, and hydrogen peroxide with distilled water rinses between each soaking treatment.[35]

General Procedure for Oxidations.—The stock solution of peroxyacetic acid (~35%) was diluted to 10% weight concentration by glacial acetic acid. The substrate (12 mmol) was dissolved in 25 ml (27 g) of 10% peroxyacetic acid (36 mmol), and the oxidation was allowed to proceed in a constant-temperature bath at 25°. The oxidations were run in the dark, but oxygen was not excluded. Use of freshly prepared peroxyacetic acid kept the hydrogen peroxide concentration below 0.3%. Aliquots (1.0 ml) were removed for stoichiometry determinations, and the unreacted peroxyacetic acid and hydrogen peroxide were analyzed by an iodimetric procedure;[36] unreacted substrate was measured by glc using an internal standard. Control runs without substrate allowed estimation of the decomposition of peroxyacetic acid so that the appropriate correction could be made in stoichiometry calculations; this correction only amounted to 10% of the initial oxidant concentration after 48 hr.

The oxidations were stopped at various times by addition of acetaldehyde (15 ml) to reduce the remaining oxidant. The reaction mixture was then neutralized, under a stream of nitrogen, to pH 8 (sodium carbonate), and the neutral products were removed by extraction (ether). The remaining alkaline layer was acidified (pH 2, HCl) and concentrated *in vacuo* at 50° to dryness; water was added; and the concentration was repeated to remove as much acetic acid as possible. The resulting product mixture was dissolved in a minimum of distilled water and extracted by ether in a continuous extractor for 24 hr to obtain an ether solution of the acidic products.

The dried ($MgSO_4$) ether extract containing the neutral products was then concentrated to about 10 ml and analyzed directly by glc with column A at 120 ml/min He and temperature programming from 100 to 160° at 2 deg/min. The ether extract containing the acidic products was dried ($MgSO_4$) and concentrated, and the resulting yellow syrup was silylated[37] with bis(trimethylsilyl)trifluoroacetamide (Regisil, Regis Chemical Co.). Glc analysis was performed with column B (165°, 75 ml/min He) using the TMS derivative of adipic acid as the internal standard. The acidic products were methylated (5% HCl in methanol) to permit collection of the pure methyl esters from column C.

4-Methylpyrocatechol Oxidation.—4-Methylpyrocatechol (I) was oxidized by the general procedure described above except that the reaction solution was initially cooled due to the exothermic nature of the oxidation. The reaction was complete within 1 hr. A precipitate which was formed during the reaction was identified as *cis,trans*-β-methylmuconic acid (VI, 2%): mp 179–182° (lit. mp 178–179°[4], 179°[6]); ir (KBr) 2680 (m), 2590 (m) (broad, carboxyl OH), 1685 (vs, C=O), 1623 (ms), 1594 cm^{-1} (ms, C=C); nmr (dimethyl-d_6 sulfoxide) δ 2.04 (d, 3 H, J = 1.5 Hz, β-CH_3), 6.00 (m, 1 H, J = 1 Hz, α-vinyl H), 6.18 (doublet of doublets, 1 H, J = 16, 1 Hz, α′-vinyl H), 8.48 (doublet of doublets, 1 H, J = 16, 1 Hz, β′-vinyl H), and *ca.* 12.1 ppm (very broad, –COOH).

The other products found were all carboxylic acids, and they were isolated by preparative gas chromatography of their methyl esters. Yields reported are average values, and were determined by glc analysis of the trimethylsilyl derivatives. The major product was γ-carboxymethyl-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (VII, 36%); its identity was established by comparison of the infrared and nmr spectra of its methyl ester derivative with the corresponding spectra of the methyl ester of the authentic lactone acid. The methyl ester of γ-carboxymethyl-γ-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (VIII-E, 4%) was also collected by glc and was identified by spectral data: ir (neat) 1755 (s, C=O), 1610 (w, C=C), 820 cm^{-1} (m, *cis*-HC=CHC=O); nmr ($CDCl_3$) δ 1.57 (s, 3 H, γ-CH_3), 2.70 (d, 1 H, J = 15.5 Hz, HCH in an AB pattern), 2.92 (d, 1 H, J = 15.5 Hz, HCH in an AB pattern), 3.68 (s, 3 H, ester CH_3), 6.03 (d, 1 H, J = 5.5 Hz, α-vinyl H), 7.65 ppm (d, 1 H, J = 5.5 Hz, β-vinyl H); mass spectrum (70 eV) *m/e* (rel intensity) parent ion 170 (4), 155 (4), 139 (4), 113 (20), 111 (5), 110 (6), 98 (9), 97 (100), 69 (32), 59 (14), 43 (49).

The dimethyl derivative of γ-carboxymethyl-γ-hydroxy-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone (IX-E, 5%) was also isolated after methylation of a product mixture followed by glc. Its structure was assigned primarily on the basis of spectral evidence: ir (neat) 1770 (vs), 1740 (vs, C=O), 1660 cm^{-1} (m, C=C); nmr ($CDCl_3$) δ 2.04 (d, 3 H, J = 1.5 Hz, β-CH_3), 2.88 (d, 1 H, J = 15 Hz, HCH in an AB pattern), 3.08 (d, 1 H, J = 15 Hz, HCH in an AB pattern), 3.17 (s, 3 H, γ-OCH_3), 3.63 (s, 3 H, ester CH_3), and 5.96 ppm (quartet, 1 H, J = 1.5 Hz, α-vinyl H); mass spectrum (70 eV) *m/e* (rel intensity) parent ion 200 (1.6), 169 (15), 127 (100), 99 (31), 68 (28), 59 (34). This oxidation product (IX) was observed to decarboxylate on the gas chromatograph to give β,γ-dimethyl-γ-hydroxy-$\Delta^{\alpha,\beta}$-butyrolactone (X): ir (neat) 3270 (s, OH), 1735 (vs, C=O), 1657 cm^{-1} (m, C=C); nmr ($CDCl_3$) 1.64 (s, 3 H, γ-CH_3), 2.08 (d, 3 H, J = 1.5 Hz, β-CH_3), 4.08 (broad, 1 H, disappears after addition of D_2O, OH), 5.73 ppm (quartet, 1 H, J = 1.5 Hz, α-vinyl H). The presence of the γ-hydroxylactone (IX) could not be demonstrated by silylation of the product mixture since it is apparently unstable to these conditions. Thus, the reported yield is based on quantitative glc analysis of the methyl ester (IX-E).

4-Methyl-*o*-benzoquinone (XI) Oxidation.—The oxidation was carried out by the general procedure, and the reaction was instantaneous. No significant amounts of volatile oxidation products were found. The acidic products were estimated as their trimethylsilyl derivatives and included *cis,trans*-β-methylmuconic acid (VI, 19%), β-methyl lactone (VII, 44%) and γ-methyl lactone (VIII, 8%). Identification was assured by comparison of retention times of the methylated and the silylated derivatives with those of authentic samples. Analysis of a product mixture after a 26-hr reaction period showed lower yields of VI (4%), VII (33%), and VIII (4%) and revealed at least three other unknown acids which were not detectable at the shorter reaction time.

4-Methylveratrole Oxidation.—The oxidation of 4-methylveratrole (II) was performed as described in the general pro-

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cedure. After a 30-hr reaction period, approximately 85% of the substrate had been oxidized. Dilution of the product mixture with water precipitated a yellow solid. Recrystallization from methanol gave thin yellow platelets of 2-methoxy-5-methyl-*p*-benzoquinone (XII, 17%): mp 174–176° (lit. mp 175–176° [9]); ir (KBr) identical with Sadtler spectrum no. 22030,[38] 1675 (s), 1653 (s), 1605 cm^{-1} (vs, C=CC=O); nmr ($CDCl_3$) 2.07 (d, 3 H, J = 1.5 Hz, CH_3), 3.83 (s, 3 H, OCH_3), 5.96 (s, 1 H, C-3 H), 6.57 ppm (quartet, J = 1.5 Hz, C-6 H). Methylation or silylation followed by glc confirmed the presence of the β-methyl lactone (VII, 7%), γ-methyl lactone (VIII, 1%), and the γ-hydroxy lactone (IX, 1%) as well as traces of unidentified products. The three lactones were verified as products by comparison of their glc retention times and their infrared spectra with those of authentic materials.

***p*-Cresol Oxidation.**—The general procedure was employed for this oxidation. Product analysis revealed that only 70% of the *p*-cresol (III) had been oxidized after 55 hr. The acidic products included *cis,trans*-β-methylmuconic acid (VI, 0.5%), β-methyl lactone (VII, 19%), γ-methyl lactone (VIII, 3%), and γ-hydroxy lactone (IX, 4%). These products were identified by comparison of their ir spectra and glc retention times (of the methyl and trimethylsilyl derivatives) with those of authentic materials.

The original ether extract of the reaction mixture (after sodium carbonate addition) yielded a neutral component, 4-hydroxy-4-methyl-2,5-cyclohexadienone (XIII, 12%): ir (neat) 3400 (ms, OH), 1660 (vs, C=O), 1630 (ms), 1617 (ms, C=C), 855 cm^{-1} (s, *cis*-CH=CH); nmr ($CDCl_3$) δ 1.48 (s, 3 H, CH_3), 3.07 (broad, 1 H, disappears on D_2O addition, OH), 6.13 (d, 2 H, J = 10 Hz, vinyl Hs α to carbonyl), 6.95 ppm (d, 2 H, J = 10 Hz, vinyl Hs β to carbonyl); mass spectrum (70 eV) m/e (rel intensity) parent ion 124 (33), 109 (100), 96 (46), 81 (58), 55 (23), 43 (36), and 27 (28). This compound has been reported to form during hydrogen peroxide oxidation of *p*-cresol.[29]

It was discovered that the acetaldehyde used to reduce the residual peroxyacetic acid diverted some of the dienone product to an acetal adduct. On the basis of infrared, nmr, decoupling experiments, and mass spectral analysis the probable structure is 6,8-dimethyl-3-keto-$\Delta^{4,5}$-7,9-dioxabicyclo[4.3.0]nonane. Since this adduct was unambiguously shown to result from reaction of dienone XIII with acetaldehyde, the yield of dienone was corrected according to the amount of acetal adduct observed.

***p*-Methylanisole Oxidation.**—*p*-Methylanisole (IV) was oxidized according to the general procedure, and only 45% of it was consumed by peroxyacetic acid in 72 hr. Dilution with water gave a yellow precipitate of 2-methoxy-5-methyl-*p*-benzoquinone (XII, 16%) which gave an ir spectrum identical with that of an authentic sample. Analysis of the neutral products from the initial ether extract showed that 4-hydroxy-4-methyl-2,5-cyclohexadienone (XIII, 16%) was formed as shown by glc retention time and ir spectral comparisons with the authentic product obtained from *p*-cresol oxidation. Another neutral product was collected at the exit of the gas chromatograph and found to be 2-hydroxy-*p*-methylanisole (XIV, 2%); the compound's infrared spectrum was identical with the spectrum of an authentic sample.[39] Glc retention times and infrared spectra of the methyl esters of the carboxylic acid products showed that they were the ester derivatives of *cis,trans*-β-methylmuconic acid (VI, 0.2%), β-methyl lactone (VII, 7%), γ-methyl lactone (VIII, 1%), and γ-hydroxy lactone (IX, 2%).

A similar reaction in which the oxidation was quenched at an earlier time (30 hr, 25% of the substrate had reacted) gave the same reaction products except that 2-hydroxy-*p*-methylanisole was formed in higher yield (6%).

2-Methoxy-*p*-cresol Oxidation.—The general procedure was used for the oxidation of 2-methoxy-*p*-cresol (V). No products were found in the initial ether extract when the reaction had consumed 85% of the substrate (24 hr). The acidic products included *cis,trans*-β-methylmuconic acid (VI, 0.4%), β-methyl lactone (VII, 9%), γ-methyl lactone (VIII, 2%) and the γ-hydroxy lactone (IX, 13%); these were identified on the basis of glc retention times of their methyl and trimethylsilyl esters.

Mesitylene Oxidation.—Oxidation of mesitylene by the general procedure gave hydroxymesitylene which was collected by preparative glc; its infrared spectrum was identical with the infrared spectrum of an authentic sample. Other products were also formed but were not identified.

Product Stability.—When 2-methoxy-5-methyl-*p*-benzoquinone (XII, 0.43 g, 2.8 mmol) was mixed with 25 ml of 7% peroxyacetic acid (1.76 g, 23 mmol), 36% of the substrate reacted in 50 hr consuming approximately an equimolar amount of oxidant. Product analysis efforts were unsuccessful.

Separate control reactions were carried out with *cis,trans*-β-methylmuconic acid (VI), β-methyl lactone (VII), and its methyl ester using 5–8% solutions of peroxyacetic acid for extended periods of time (24–72 hr). Peroxyacetic acid was not consumed by these substrates. Good recoveries (80–85%) were obtained of β-methyl lactone (VII) after the entire work-up procedure. On the other hand, *cis,trans*-β-methylmuconic acid was recovered in only 47% yield (as β-methyl lactone).

Effect of Methyl Methacrylate.—An oxidation of *p*-cresol (III) was carried out in the usual manner except that methyl methacrylate (3.3% by weight) was added to the reaction. The rate of peroxyacetic acid consumption was the same in this reaction as with an oxidation carried out without methyl methacrylate. Product analysis showed no significant differences which could be ascribed to the presence of the monomer.

Registry No.—I, 452-86-8; II, 494-99-5; III, 106-44-5; IV, 104-93-8; V, 93-51-6; VI, 31659-59-3; VII, 6307-98-8; VII-E, 31656-70-9; VIII-E, 31656-71-0; IX-E, 31656-72-1; X, 14300-89-1; XI, 3131-54-2; XII, 614-13-1; XIII, 23438-23-5; peroxyacetic acid, 79-21-0.

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