k_{OH} is the second-order coefficient for the formation of 2,4-dinitrophenol and equals k_ψ(fractional yield of 2,4-dinitrophenol)/(HO^-).

Acknowledgments. Research was supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina. A.B.P. is a grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas. We thank Professor Claude F. Bernasconi for critical reading of the manuscript and helpful suggestions.

Registry No.—1-Fluoro-2,4-dinitrobenzene, 7-34-8; imidazole, 288-32-4; aniline, 62-53-3; 2,4-dinitrophenylimidazole, 14545-01-8; 2,4-dinitrophenol, 51-28-5.

References and Notes

(1) C. F. Bernasconi, *MTP Int. Rev. Sci.: Org. Chem., Ser. One*, **3**, 33 (1973).
(2) J. F. Bunnett and C. F. Bernasconi, *J. Am. Chem. Soc.*, **87**, 5209 (1965).
(3) C. F. Bernasconi, *J. Org. Chem.*, **32**, 2947 (1967).
(4) J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958).
(5) C. F. Bernasconi, R. H. de Rossi, and P. Schmid, *J. Am. Chem. Soc.*, **99**, 4090 (1977).
(6) Earlier interpretations of general base catalysis in terms of a rapid proton transfer equilibrium and a rate limiting, *general acid catalyzed* k_4 step have been shown to be unattractive in protic solvents,[5] although they are valid in aprotic solvents.[7]
(7) J. A. Orvik and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 2417 (1970).
(8) A. J. Kirby and W. P. Jencks, *J. Am. Chem. Soc.*, **87**, 3209 (1965).
(9) A. J. Kirby and M. Jounas, *J. Chem. Soc. B*, 1187 (1970).
(10) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).
(11) (a) J. F. Bunnett and R. H. Garst, *J. Am. Chem. Soc.*, **87**, 3875 (1965); (b) D. M. Brewis, N. B. Chapman, J. S. Paine, J. Shorter, and D. J. Wright, *J. Chem. Soc., Perkin Trans. 2*, 1787 (1974).
(12) C. F. Bernasconi and C. L. Gehriger, *J. Am. Chem. Soc.*, **96**, 1092 (1974).
(13) W. P. Jencks, *J. Am. Chem. Soc.*, **94**, 4731 (1972).
(14) R. H. de Rossi, unpublished results.
(15) D. G. Oakenfull, K. Salvesen, and W. P. Jencks, *J. Am. Chem. Soc.*, **93**, 188 (1971).
(16) R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970).
(17) H. Walba and R. W. Isensee, *J. Am. Chem. Soc.*, **77**, 5488 (1955).
(18) N. Gravitz and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 499 (1974).
(19) C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 780 (1969).
(20) C. A. Bunton and L. Robinson, *J. Org. Chem.*, **35**, 733 (1970).
(21) J. F. Bunnett and C. F. Bernasconi, *J. Org. Chem.*, **35**, 70 (1970).
(22) P. Salomaa, A. Kankaanpera, and M. Lahti, *J. Am. Chem. Soc.*, **93**, 2084 (1971).
(23) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).
(24) E. Buncel and W. Eggimann, *J. Am. Chem. Soc.*, **99**, 5958 (1977).
(25) C. F. Bernasconi and F. Terrier, *J. Am. Chem. Soc.*, **97**, 7458 (1975).
(26) C. F. Bernasconi and H. Wang, *J. Am. Chem. Soc.*, **99**, 2214 (1977).
(27) E. Buncel, J. Webb, and J. F. Wiltsshire, *J. Am. Chem. Soc.*, **99**, 4429 (1977).
(28) L. F. Fieser, "Experiments in Organic Chemistry", 2nd ed, D. R. Heath, Boston, 1941, p 360.
(29) R. H. de Rossi and R. A. Rossi, *J. Org. Chem.*, **39**, 3486 (1974); R. H. de Rossi, R. A. Rossi, and F. N. R. Gimenez, *ibid.*, **41**, 3163 (1976).

Some Unusual Oxidation Products of 2,6-Di-*tert*-butyl-4-methylphenol[1]

Ben M. Benjamin,* Vernon F. Raaen, Edward W. Hagaman, and Lloyd L. Brown

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Received January 20, 1978

The potassium permanganate oxidation of 2,6-di-*tert*-butyl-4-methylphenol (**1**), adsorbed on a stationary Celite phase, gives several interesting monomeric products in low yields. These products were identified primarily by ^{13}C and ^1H NMR. The products of oxidation of **1** with performic acid and also with oxygen in alkaline ethanol are related and their structures and NMR spectral features are also discussed.

We have been interested in devising a method for oxidizing coal while simultaneously removing the aqueous base-soluble oxidation products from further reaction with the oxidizing agent. In batch processes the fragments cannot be protected from contact with fresh oxidizing agent. Because some coals are, at least partly, phenolic substances,[2,3] we believe that the oxidation fragments derived from the coals in ordinary batch processes may undergo coupling reactions typical of phenols.[4,5] The idea that phenol coupling reactions can lead to erroneous conclusions concerning the structure of coal was expressed earlier by Yohe.[6] Such coupling reactions lead to highly substituted aromatic molecules which ultimately may be broken down to mellitic acid and benzene pentacarboxylic acid, not accurately reflecting the lower degree of aromatic substitution in untreated coal. In our experiments[7] with coal, no mellitic acid could be isolated. Reactions other than coupling, e.g., hydroxylations, ketonizations, and rearrangements, can also occur under strongly basic conditions and a representative product distribution should reflect these reactions. Any interpretation of coal structure, based on oxidation studies, must take into account these chemical transformations. In consideration of these remarks, in part, we undertook a comparative study of the oxidation of 4-methyl-2,6-di-*tert*-butylphenol[7] (**1**) (BHT) by our method and by the batch method. The purpose of this paper is to describe the structures of some of the neutral, ether-soluble compounds isolated from these reactions.

The batch oxidation procedure of **1** using permanganate initially gives coupled or dimeric products which with an excess of oxidizing agent are converted to acids and carbon dioxide. Our procedure gives mostly acids, some of which we could not identify, and a small yield of neutral monomeric oxidation products. In attempting to independently synthesize some of these compounds, we prepared intermediates by oxidizing **1** with performic acid as well as with oxygen in the presence of alcoholic potassium hydroxide. Structures of the minor products of these reactions are described also.

Our procedure for oxidizing coal[7] consists of grinding it to a fine powder in an inert atmosphere and mixing it intimately with Celite. The mixture is then placed in a chromatographic column, and a solution of potassium permanganate is percolated by gravity feed through the contents of the column. The effluent, which contains the oxidation products, is collected for analysis of its contents. Using this procedure, oxidation takes place in a narrow, well-defined zone. The oxidizing agent is exhausted in that zone and the soluble products which are formed are eluted through the column away from exposure to more oxidizing agent.

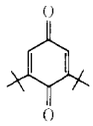
Experimental Section

General. 2,6-Di-*tert*-butyl-4-methylphenol was purchased from Aldrich Chemical Co. It was better than 99% pure as determined by GC analysis. It was used as received. Melting points were determined on a Koffler hot bench. IR spectra were determined in CCl_4 solution on a Beckmann IR-8 infrared spectrometer. Carbon–hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

NMR spectra were recorded on a Varian XL-100-15 NMR spectrometer. Chemical shifts of the ^1H NMR spectra were measured

0022-3263/78/1943-2986$01.00/0

Table I. ^{1}H NMR Data for Oxidation Products

compd[a]	registry no.	solvent[b]	δ, ppm (Me_4Si = 0) $C(CH_3)_3$	$C(CH_3)_3$	CH_3	CH	CH	OH[c]
3a		Me_2SO-d_6	0.97 (9 H, s)	1.02 (9 H, s)	2.29 (3 H, s)	2.73 (1 H, d)	4.52 (1 H, d)	3.31 (1 H, s)
		$CDCl_3$	1.05 (9 H, s)	1.09 (9 H, s)	2.36 (3 H, s)	2.72 (1 H, d, J = 4.85 Hz)	4.51 (1 H, d, J = 4.85 Hz)	3.59 (1 H, s)
3b		$CDCl_3$	1.03 (9 H, s)	1.07 (9 H, s)	2.37 (3 H, s)	2.52 (1 H, d, J = 8.85 Hz)	4.55 (1 H, d, J = 8.85 Hz)	3.00 (1 H, s)
4	66483-18-9	Me_2SO-d_6	1.01 (9 H, s)	1.15 (9 H, s)	1.04 (3 H, s)		7.04 (1 H, s)	5.01 (2 H, b)
		$CDCl_3$	1.03 (9 H, s)	1.20 (9 H, s)	1.30 (3 H, s)		7.04 (1 H, s)	1.67 (1 H, s) 2.88 (1 H, s)
5	66483-17-8	$CDCl_3$	1.14 (18 H, s)		1.35 (3 H, s)		3.62 (1 H, s)	3.35 (1 H, s) 4.18 (1 H, s)
6	66483-16-7	C_6D_5N	1.20 (9 H, s)	1.26 (9 H, s)	1.47 (3 H, s)	3.97 (1 H, s)	4.83 (1 H, s)	5.95 (3 H, b)
		$CDCl_3$	0.98 (9 H, s)	1.09 (9 H, s)	1.01 (3 H, s)	3.53 (1 H, s)	4.24 (1 H, d, J = 10.0 Hz)	2.91 (1 H, s) 2.92 (1 H, d, J = 10 Hz) 3.55 (1 H, s)
7	66483-15-6	C_6D_5N	1.15 (9 H, s)	1.27 (9 H, s)	1.74 (3 H, s)	4.10 (1 H, s)	6.75 (1 H, s)	4.85 (2 H, b) 6.10 (1 H, b)
		$CDCl_3$	0.94 (9 H, s)	1.24 (9 H, s)	1.47 (3 H, s)	3.80 (1 H, d, J = 6.5 Hz)	6.43 (1 H, s)	2.52 (1 H, b) 3.71 (1 H, d, J = 6.5 Hz) 3.93 (1 H, s)
10	13693-18-0	$CDCl_3$	1.18 (21 H, s)	1.40 (18 H, s)	1.40 (CH_3) 2.75 (CH_2, 2 H, s)	6.53 (2 H, s)	6.83 (2 H, s)	5.05 (1 H, s)
11	10396-80-2	$CDCl_3$	1.22 (18 H, s)		1.40 (3 H, s)	6.54 (2 H, s)		2.45 (1 H, s)
12	14387-13-4	$CDCl_3$	1.25 (18 H, s)	1.42 (18 H, s)	1.59 (3 H, s)	6.54 (2 H, s)	7.03 (2 H, s)	5.13 (1 H, s)
13	6485-57-0	$CDCl_3$	1.24 (18 H, s)		1.37 (3 H, s)	6.60 (2 H, s)		8.30 (1 H, s)
14	52922-83-5	$CDCl_3$	1.11 (9 H, s)	1.15 (9 H, s)	1.36 (3 H, s)	3.55 (1 H, d, J = 3.0 Hz)	6.08 (1 H, d, J = 3.0 Hz)	2.9 (1 H, s)
15	52922-87-9	$CDCl_3$	1.04 (18 H, s)		1.36 (3 H, s)	3.38 (2 H, s)		3.04 (1 H, s)
16	51033-92-2	$CDCl_3$	1.24 (21 H, s)		1.24	6.48 (2 H, s)		
17	66483-14-5	$CDCl_3$	0.96 (9 H, 2)	1.20 (9 H, s)	2.07 (3 H, s)	3.00 (2 H, s, CH_2)	7.78 (1 H, s)	
	719-22-2	$CDCl_3$	1.28 (18 H, s)			6.49 (2 H, s)		

[a] Compounds with low chloroform solubility were initially recorded in alternate solvents as indicated. [b] Because of the small amounts of compounds available, pyridine-d_5 was used as solvent for obtaining ^{1}H NMR so that the materials could be recovered easily. [c] Identification of OH peaks was accomplished by recording the spectrum before and after shaking the sample with a drop of D_2O. δ is concentration dependent.

relative to internal Me_4Si. Chemical shifts of ^{13}C NMR spectra were measured relative to the central peak of the solvent, either chloroform-*d* or dimethyl-d_6 sulfoxide, and are expressed on the Me_4Si scale: δ^{Me_4Si} and δ^{CDCl_3} + 76.9 ppm = $\delta^{Me_2SO\text{-}d_6}$ + 39.5 ppm.

Column Oxidation Procedure. The compound 2,6-di-*tert*-butyl-4-methylphenol (**1**, 50 g) was dissolved in the minimum amount of CH_2Cl_2 and the solution was mixed with 400 g of Hyflo Super-Cel Celite. The mixture was made homogeneous by stirring it and then tumbling it in a ball mill for 2 h. Solvent was removed under vacuum. The Celite–phenol mixture was placed in a Pyrex tube (4 cm × 125 cm) which contained a coarse fritted glass disk at the bottom. Potassium permanganate solution was poured into the top of the column and allowed to percolate through the column contents. As oxidation occurred, a deposit of manganese dioxide formed. The temperature in the oxidation zone was 35–40 °C. The solution, which was depleted in oxidizing agent and no longer contained the permanganate color, seeped down the column, below the oxidation zone, and eventually was collected for further processing. When the manganese dioxide had formed all the way to the bottom of the column, no more effluent was collected.

Separation of Products. The aqueous alkaline solution, approximately 4 L, collected from the foregoing oxidation procedure, was extracted continuously with ether for 48 h. After careful evaporation of the ether, there remained 2.5 g (5%) of an oily liquid. The liquid was separated into two fractions by vacuum distillation at 50 °C and 0.05 mm. The residue was saved for later processing and the volatile fraction was redistilled at 0.05 mm and ambient temperatures to give 3,3-dimethyl-1-hydroxybutan-2-one (**2**): IR 3440, 2950, 1675 (broad); ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9 H), 3.3 (broad, 1 H), 4.41 (s, 2 H). The resonance at δ 3.3 disappeared after the sample was shaken with D_2O. Compound **2** was reduced with $LiAlH_4$ and the product of reduction was treated with *p*-nitrobenzoyl chloride in pyridine. The resulting ester was crystallized from ethanol, mp 142 °C. The ^{1}H NMR spectrum was consistent with that expected for the di-*p*-nitrobenzoate ester of 3,3-dimethylbutane-1,2-diol.

A chromatographic column (130 cm × 2 cm) containing 100 g of Fischer alumina, wet with hexane, was prepared. The residue saved from the foregoing distillation was dissolved in hexane, 10 mL, and the solution was placed on top of the alumina. The compounds were eluted with several ether–hexane mixtures followed by pure ether and finally 0.5% methanol in ether. Eluent was collected in 100-mL fractions. The solvent was evaporated from each fraction and the residue was weighed. Elution with solvent of each composition was continued until the residue in a 100-mL fraction weighed less than 5 mg. The six compounds described in the following paragraphs were recovered from the residues; no pure substance could be recovered from the intermediate oily fractions: ^{1}H NMR data are presented in Table I and ^{13}C NMR data are given in Tables II and III.

3-Oxo-2-hydroxy-5-acetyl-2,4-di-*tert*-butyltetrahydrofuran (3a). The residue, 0.44 g, recovered by elution of the column with 5% ether in hexane was crystallized three times from hexane: mp 124 °C; IR (CCl_4) 3600, 3400, 1750, and 1720 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 66.02; H, 9.29.

Compound **3b**, an epimer of **3a**, was not isolated. It formed as a mixture with **3a** when **3a**, in $CDCl_3$ solution, was treated with $Eu(DPM)_3$ shift reagent or with NaOH solution. **3b** could be detected by ^{1}H NMR, in small quantities, in several of the chromatographic fractions.

Table II. ^{13}C Chemical Shifts of 1[e] and its Symmetrical Oxidation Products[a]

	1	8[f]	9[g]	10	11	12	13	15	16	18[h]
C(1)	151.3	151.5	186.1	186.0	185.7	186.3	186.0	198.8	186.2	128.5
C(2)	135.5	135.4	149.9[b]	145.5	145.1	143.7	148.2	66.2	147.2	127.4
C(3)	125.3	124.7	124.2	146.4	143.0	147.3	140.1	66.3	140.8	136.3
C(4)	128.0	132.5	135.9	40.9	67.3	43.3	78.5	68.0	76.8	159.5
C(5)	125.3	124.7	134.0[c]	146.4	143.0	147.3	140.1	66.3	140.8	136.3
C(6)	135.5	135.4	149.6[b]	145.5	145.1	143.7	148.2	66.2	147.2	127.4
C(7)	21.2	38.0	133.2[c]	26.3	28.0	24.4	23.9	22.4	24.2	191.4
t-Bu	30.4 (34.2)	30.4 (34.2)	29.6 (35.4[d]) 29.6 (35.8[d])	29.4 (34.4)	29.4 (34.5)	29.5 (34.6)	29.4 (34.7)	25.9 (33.1)	29.5 (34.7)	30.0 (34.3)
C(1′)				127.5		131.7				
C(2′)				126.2		122.7				
C(3′)				134.9		135.6				
C(4′)				152.2		152.3				
C(5′)				134.9		135.6				
C(6′)				126.2		122.7				
C(α)				48.0						
C(3′)-*t*-Bu				30.2 (34.1)		30.3 (34.6)				
C(5′)-*t*-Bu				30.2 (34.1)		30.3 (34.6)				

[a] Recorded in chloroform-*d* solution. [b,c,d] Signals within any vertical column may be reversed. [e] Registry no. 128-37-0. [f] Registry no. 1516-94-5. [g] Registry no. 809-73-4. [h] Registry no. 1620-98-0.

Table III. ^{13}C Chemical Shifts of Unsymmetrical Oxidation Products[a]

	3a	3b[a]	4[b]	5[a]	6[b]	7[b]	14[a]	17[a]
C(1)			206.9	198.9	208.5	202.5	195.9	
C(2)	100.9	101.6	148.1	81.9	70.3	149.3	143.0	170.1
C(3)	208.7	204.6	157.8	209.0	64.7	143.1	139.0	128.9
C(4)	52.9	55.7	78.5	70.5	68.3	68.3	68.6	203.2
C(5)	81.2	79.8	88.8	63.8	70.2	70.0	61.4	91.1
C(6)	209.8	209.7	28.4	77.0	80.6	79.1	66.0	45.0
C(7)	26.6	26.5		21.4	18.7	26.6	26.0	204.6
C(8)								31.2
C(2)-*t*-Bu	24.4 (36.7)	24.0 (36.9)	27.9[c] (31.1)	25.8[c] (31.4)[d]	25.7[c] (32.3)	29.7 (34.1)	29.2 (34.5)	
C(3)-*t*-Bu								28.0 (29.5)
C(4)-*t*-Bu	27.9 (34.2)	27.7 (32.4)		26.0[c] (32.7)[d]				
C(5)-*t*-Bu			27.0[c] (37.6)					24.3 (37.4)
C(6)-*t*-Bu					25.6[c] (40.3)	25.5 (38.4)	26.0 (32.1)	

[a] In chloroform-*d* solution. [b] In dimethyl-d_6 sulfoxide solution. [c,d] Signals within any vertical column may be reversed.

4,5-Dihydroxy-4-methyl-2,5-di-*tert*-butylcyclopent-2-en-1-one (4) was recovered from 90 mg of partly crystalline material obtained when a mixture of 10% ether in hexane was passed through the column. It was crystallized from a chloroform–hexane mixture: mp 197 °C (capillary); IR (CCl_4) 3600, 3550, and 1695 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.01. Found: C, 69.91; H, 9.74.

4,5-Oxa-2,6-dihydroxy-6-methyl-2,4-di-*tert*-butylcyclohexane-1,3-dione (5). A single crystal of **5** (215 mg) was obtained when the column eluant (20% ether in hexane) was allowed to spontaneously evaporate. The structure of the compound was determined by X-ray crystallography: [18]mp 107 °C; IR (CCl_4) 3520, 1740, and 1730 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.88; H, 8.30. A partly crystalline fraction (0.125 g) was recovered when 30% ether in hexane was passed through the column. After three crystallizations from hexane, 15 mg of a pure solid of undetermined structure remained, mp 154 °C: ^1H NMR ($CDCl_3$) δ 1.03 (9 H, s), 1.08 (9 H, s), 1.44 (3, H, s), 4.43 (1 H, s), 5.29 (1 H, s), 2.92 (5 H, 2, OH). Anal. Calcd for $C_{15}H_{28}O_6$: C, 59.19; H, 9.27. Found: C, 59.79; H, 8.82.

2,3-Oxa-4-methyl-4,5,6-trihydroxy-2,6-di-*tert*-butylcyclohexan-1-one (6) was recovered when 50% ether in hexane was used as an eluant. It was crystallized from a chloroform–hexane mixture: mp 193 °C; IR (CCl_4) 3580, 3560, 3500, 3380, and 1695 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 62.92; H, 9.47.

4,5,6-Trihydroxy-4-methyl-2,6-di-*tert*-butylcyclohex-2-en-1-one (7). When ether was used as an eluant, 177 mg of a crystalline material was recovered. It was recrystallized from pentane: mp 132 °C; IR (CCl_4) 3560, 3940, and 3680 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.77; H, 9.91.

The acid fraction (~45 g) contained formic, acetic, and pivalic acids as expected. It also contained a mixture of other keto and hydroxy acids from which no pure compounds could be separated.

Batch Oxidation Procedure. Potassium permanganate solution, 48 g, in 1 L of water was added to a stirred suspension of BHT (50 g) in 200 mL of acetone. The oxidation mixture was cooled in an ice bath to prevent the temperature from rising above 20 °C. After all the $KMnO_4$ was consumed, manganese dioxide was dissolved by adding $NaHSO_3$, and the neutral organic materials were recovered from the reaction mixture by extracting it with ether. The ether was evaporated and hexane was added to the pasty solid. The solid was collected on a filter. It consisted mostly of a mixture of the two dimers of the starting phenol,[9] 4,4′-ethylenebis[2,6-di-*tert*-butylphenol] (**8**) and 2,2′,6,6′-tetra-*tert*-butyl-1,1′-stilbenequinone (**9**). The oily portion of the oxidation product was chromatographed on alumina as described above. Small amounts of **3, 5,** and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**18**)[9] were isolated. Approximately 15% of the oily fraction was the dimer,[10] 2,6-di-*tert*-butyl-4-(3′,5′-di-*tert*-butyl-4′-hydroxybenzyl)-4-methyl-2,5-cyclohexadien-1-one (**10**), mp 116 °C. ^1H NMR data are given in Table I. Small amounts of other compounds could not be purified nor characterized.

The oxidation of 4-methyl-2,6-di-*tert*-butylphenol (1) with oxygen in the presence of alcoholic potassium hydroxide was done according to the method of Kharasch and Joshi.[11] After 4-methyl-4-hydroxy-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (**11**), mp 113–114 °C, was isolated from the reaction products by crystallization from hexane, solvent was evaporated from the mother liquors and the pasty residue was chromatographed on alumina as described above. A small amount of starting phenol was recovered by eluting the column with hexane. When the column was eluted with 5% ether in hexane, the dimeric compound, 2,6-di-*tert*-butyl-4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-4-methylcyclohexa-2,5-dien-1-one (**12**), mp 159 °C, was isolated:[12] IR (CCl_4) 3630, 1658, and 1630 cm^{-1}. Anal. Calcd for $C_{29}H_{44}O_2$: C, 82.02; H, 10.45. Found: C, 82.30; H, 10.98. Compound **11** was eluted from the column with 20% ether in hexane and the corresponding hydroperoxide, **13**, mp 119–120 °C, was eluted

with 50% ether in hexane. Pure ether was used to elute the monoepoxy compound,[13] 5,6-oxa-4-methyl-4-hydroxy-2,6-di-*tert*-butylcyclohex-2-en-1-one (**14**), mp 108 °C from pentane: IR (CCl_4) 3585, 3495, 3390, 1665, and 936 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.61; H, 9.70. Finally, 5% methanol in ether was used to elute the diepoxy compound,[13] 2,3-5,6-dioxa-4-methyl-4-hydroxy-2,6-di-*tert*-butylcyclohexan-1-one (**15**), mp 134 °C, from hexane: IR (CCl_4) 3580, 3500, 3400, 1700, and 952 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.33. Found: C, 67.13; H, 9.02.

Oxidation of 11 with Performic Acid. To a solution of 20 mL of 30% hydrogen peroxide in 80 mL of 90% formic acid was added 8 g of compound **11** and 5 mL of hexane. The reaction mixture was stirred vigorously and heated at 40 °C for 5 h. The solution was made strongly basic by the addition of 20% sodium hydroxide. The organic products were extracted with hexane and chromatographed on alumina as described earlier. The first hexane eluant contained a small amount of yellow crystalline 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione, mp 68 °C.[14] The next several flasks contained the new peroxy compound, bis(4-oxy-4-methyl-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one) (**16**), mp 125 °C, from ethanol: IR (CCl_4) 1660 and 1620 cm^{-1}. Anal. Calcd for $C_{30}H_{46}O_4$: C, 75.55; H, 9.85. Found: C, 75.57; H, 9.86. When the eluant was 20% ether in hexane, there was obtained a white crystalline material, 4-oxo-3,5-di-*tert*-butyl-5-(1-propan-2-one)-dihydrofuran (**17**), mp 70 °C, from hexane: IR (CCl_4) 1705, 1680, and 1600 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.02; H, 9.65. The subsequent fractions contained **11, 14, 15,** and a small amount of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**18**).

Oxidation of 11 with Osmium Tetraoxide. One gram (3.94 mmol) of osmium tetraoxide was added to 10 mL of cold pyridine. The mixture was stirred for 15 min and 0.9 g (3.8 mmol) of **11** was added. The mixture was stirred while cooling it in an ice bath for 1 h. Stirring was continued at ambient temperature for 3 h, then 1.8 g of sodium bisulfite dissolved in 30 mL of H_2O was added. After the reaction mixture was stirred for 0.5 h, 10 mL of concentrated HCl was added and the solution was extracted three times with methylene chloride. The solvent was evaporated and the product was decolorized with Norit and crystallized three times from hexane, mp 131 °C, not depressed when mixed with **7**; both had the same spectral properties.

Structure Assignment

Carbon-13 chemical shift data from proton noise-decoupled spectra, and one-bond C–H coupling patterns from single-frequency off-resonance decoupled (sford) spectra, permit a facile identification of those oxidation products which possess elements of symmetry, i.e., **8, 9, 10, 11, 12, 13, 15,** and **16** (Table II). The unambiguous chemical shift assignments of these substances form the basis for the ^{13}C NMR spectral analysis of the more complex products.

The dimerization of 2,6-di-*tert*-butyl-4-methylphenol (**1**) at the methyl group to form **8** is indicated by a β effect at C(4) (+4.5 ppm), an acyclic γ effect imposed upon the aromatic methines (−0.6 ppm),[15] and the triplet sford signal of the ethano bridge carbons of the latter.

The methyl resonance of the *tert*-butyl groups in these substances (30.4 ppm) reoccurs in the phenolic half of the "dimers" **10** and **12** and allows the *tert*-butyl resonances of the quinoid half of the latter compounds to be assigned by difference. The latter resonance, 29.4 ± 0.1 ppm, is faithfully reproduced in the quinoid monomers **11** and **13** and dimers **9** and **16.**

The structural difference between **11** and its hydroperoxide **13** is clearly indicated by the large β and γ effects suffered by C(4) and the methyl resonance, respectively. The γ effect observed on the olefinic methine, C(3), is reflected in the nearly equivalent shift of opposite sign of the distant olefinic carbon center, C(2), a behavior typical of highly polarizable double bonds.[16] In contrast to these characteristic shifts the peroxide ether **16** displays a spectrum just slightly different from that of the hydroperoxide monomer **13.** The predictably small shift differences between these substances negates their structural differentiation solely by ^{13}C NMR shift data. They are identified by the known physical constants of **13**[11] and by their proton spectra and chemical analysis. The methyl hydrogens of **13** resonate at 1.36 ppm while the signal for the methyl group of **16** is superimposed on the *tert*-butyl signal at 1.24 ppm.

The characteristic high-field carbonyl resonance of the quinoid substances, i.e., 186 ppm, the result of dienone cross conjugation, is shifted strongly downfield (198.8 ppm) in the spectrum of the diepoxide **15.** The presence of the epoxide unit is apparent from the value of $^1J_{CH}$ of the oxymethine resonance C(3)(5), i.e., 180 Hz.[17] This magnitude is typical of epoxides and is at least 25 Hz greater than found in larger oxetane rings. The methyl resonances of the *tert*-butyl groups of **15** are shifted upfield 3.6 ppm from their location in the quinoid derivatives. This shift, a γ effect due to the C(2)(6) oxygen substituent, is a sensitive monitor of the ring substitution pattern (vide infra).

The gross structure of compounds **5, 6, 7,** and **14** all of which contain 15 carbon atoms and result from partial oxidation of **1** can be fully determined by reference to the shift data of the previous symmetrical substances. Their ^{13}C NMR spectra are listed in Table III. The dissimilar *tert*-butyl group methyl signals of **14,** the presence of an α,β-unsaturated eneone moiety, and epoxide residue ($^1J_{C(3)-H}$ = 182.2 ± 0.3 Hz) are consistent with the known structure of **14.**[13]

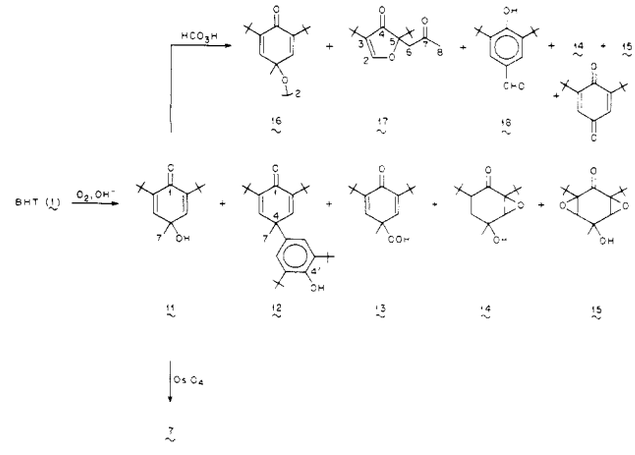
The ^{13}C spectra of **14** and **7** are equivalent with respect to the number and multiplicity of carbon resonances. The major difference between them is an approximate 10 ppm downfield shift of the two hydroxy carbon signals in the former, a change consonant with the change from the epoxide linkage to the vicinal glycol unit. Thus, **7** is a 4,5,6-trihydroxy-4-methyl-2,6-di-*tert*-butylcyclohex-2-enone, a structure independently proved by the synthesis of **7,** as outlined in Scheme I.

The preparation of precursor **11** by treatment of **1** with oxygen in alkaline solution has been reported[11] and is accompanied by the formation of hydroperoxide **13** and the 29-carbon "dimeric" product **12.** Careful workup of the crystallization liquors resulted in the isolation, in low yield, of epoxides **14** and **15**[13] whose structures are discussed in the foregoing paragraphs. Further oxidation of **11** with osmium tetroxide gives **7** in high yield. Since this oxidation generates a cis glycol from the double bond, the stereochemistry of the C(2) and C(3) substituents of **7** is certain but the relationship of these centers to the C(4) substituents remains undefined.

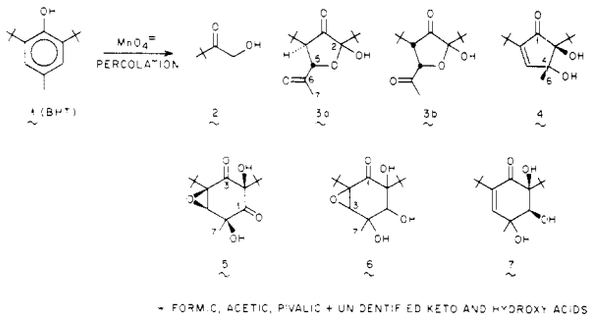
In an attempt to prepare a 2,3-trans isomer of **7, 11** was oxidized with performic acid. No glycols were obtained from the reaction. Instead, the epoxides **14** and **15** were isolated along with the four additional substances depicted in Scheme I.

The three resonances of the hydroxylated carbons of **7** also occur at almost identical shifts in the spectrum of **6,** but the olefinic signals of the former are now replaced by two addi-

Scheme I



Scheme II



tional oxygenated signals. The one-bond heteronuclear coupling of C(3), i.e., $^1J_{C(3)-H} \approx 180$ Hz, defines the new oxygenated carbons as an epoxide unit. Comparison of the methyl resonance of the *tert*-butyl groups of these two substances reveals the low field signal of **7**, 29.7 ppm, is shifted to 25.7 ppm in **6**. The near coincidence of the two *tert*-butyl groups of the latter indicates that the magnitude of the γ effect imposed on them by the C(2),(6) oxygen functions is equivalent for both functional groups.

The structure of **5** has been elucidated recently by X-ray analysis[18] and is an example of an oxidation product with fully defined stereochemistry: all oxygen functions have a cis relationship to each other. The epoxide resonances of **5** are nearly identical to those of **6**, a condition which is expected on the basis of shift correlations of simpler cyclohexanols[20] and cyclohexanones[21] if the C(5) hydroxyl group of **6** is equatorial and the relative stereochemistry of C(2), (3), (4), and (6) in **6** and **5** are the same. If **6** is the direct precursor of **5** the chemical shift correlation indicates all oxygen functions of **6** are cisoid.

In the highly oxygenated derivatives of **1**, e.g., **5** or **6**, continued oxidation results in ring opening and decarboxylation. The 14-carbon products so formed can show great structural diversity dependent on the conditions under which they were formed and isolated.

The ^{13}C NMR spectra of **3a** (Table III) reveal two saturated keto carbonyl carbons, two dissimilar *tert*-butyl groups, a methyl group, two methine carbons (one bound directly to oxygen), and a dioxygenated tetrahedral carbon. The ^1H NMR of the substance reveals the methine protons as doublets with a common coupling constant (J = 4.8 Hz), establishing their vicinal relationship, a strongly deshielded methyl resonance (δ 2.29), and one hydroxylic proton.

A chloroform solution of **3a** is converted to a ca. 1:1 epimeric mixture of **3a** and **3b** by exposure to either aqueous base or Eu(dpm)$_3$. While the ^{13}C NMR of **3b** is very similar to **3a** the ^1H NMR of the former reveals an increase in the vicinal methine coupling constant (8.85 Hz).

These data and the fact that these substances give a negative ferric chloride test establish their structures (Scheme II). The methine hydrogens in **3a** and **3b** are trans and cis, respectively, but the stereochemical relationship of these hydrogens with respect to the hemiacetal carbon substituents is not defined.

Compound **17**, a product of performic acid oxidation of **11** (see Experimental Section), possesses a heavily functionalized furan ring system. Its ^{13}C spectra reveal a highly polarized α-substituted α,β-unsaturated enone moiety, nonequivalent *tert*-butyl groups, and a tertiary oxycarbon (Table III). The remaining three resonances in its spectrum arise from a methyl (31.2 ppm), methylene (45.0 ppm), and saturated ketocarbonyl carbon (204.6 ppm). These chemical shifts indicate an acetonyl side chain and the extremely narrow triplet multiplet lines of the methylene resonance in the sford spectrum, indicative of few long-range C–H coupling interactions, suggest this function is attached to a nonprotonated site. Thus, the structure of this substance can only be represented by formula **17**.

The methyl resonances of the *tert*-butyl groups of the furanoid substances **3a, 3b,** and **17** appear at 27.8 ± 0.2 or 24.2 ± 0.2 ppm depending on the number of nonhydrogen substituents in the γ position. Both resonances are more shielded than their counterparts in the cyclohexane-based substances and are an equally effective monitor of local structure pattern.

Compound **4** is the sole isolated example of a permanganate oxidation product containing a cyclopentane ring system. The low field carbon resonances and coupling patterns in its spectra identify an α-substituted α-β-unsaturated enone array. Two tertiary oxycarbons, two *tert*-butyl groups, and an aliphatic methyl group complete the signal set. These data, in conjunction with proton resonance of the methyl group, can be accommodated by 2,5-di-*tert*-butyl-4,5-dihydroxy-4-methylcyclopent-2-en-1-one or 2,4-di-*tert*-butyl-4,5-dihydroxy-5-methylcyclopent-2-en-1-one. An X-ray crystallographic analysis[19] revealed the substance to be the former and defined the relative stereochemistry of the vicinal hydroxy groups, as shown in formula **4** (Scheme II).

Discussion

Schemes II and III summarize the product distribution obtained by permanganate oxidation of BHT (**1**) by the controlled oxidation scheme and by the batch method, respectively. The latter procedure, as is well known, results in the preponderant formation of phenol coupling products. The characterized products of controlled oxidation of 1 are monomeric species: 15-carbon compounds resulting from simple oxidation of the starting material and 14-carbon substances which result from oxidative degradation.

The first step in the oxidation of hindered phenols may be the formation of the phenoxy radical.[5] An alternative possibility is discussed by Waters.[22] Regardless of its structure, the restricted mobility and low concentration of this moiety provided by absorption on an inert support represses coupling reactions, and continued oxidation of **1a** takes precedent. In our experiments the first intermediate probably is quenched with hydroxylating species to yield a semiquinone, **11** or **13**.

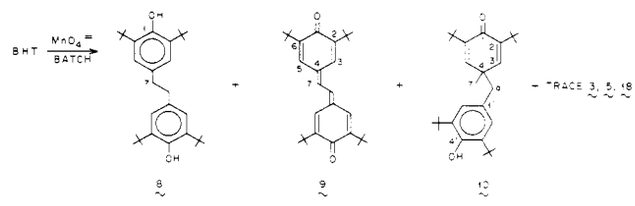
Although **11** or **13** is stable under milder oxidation[11] conditions (Scheme I), it was not detected among the products of permanganate oxidation and likely serves as the intermediate in route to the substances depicted in Scheme II.

Conclusion

The oxidation of hindered phenols can yield both dimeric and monomeric products depending on the oxidizing conditions employed. The studies described here demonstrate the diversity of compounds obtained when 2,6-di-*tert*-butyl-4-methylphenol (BHT) is oxidized. Because of the variety of products available from the oxidation of one pure phenolic compound, caution is emphasized when interpreting data from coal oxidation studies in terms of coal structure.

Besides its relationship to the structure of coal, the results reported in this paper have other implications. Considering the wide distribution of BHT as an antioxidant in many of the commodities we use daily, including food, it seems imperative

Scheme III



that we become familiar with the properties of the oxygenated derivatives of BHT.

Registry No.—**2**, 38895-88-4; **3**, 66483-19-0; 3,3-dimethyl-1,2-butanediol bis(*p*-nitrobenzoate), 66483-13-4.

References and Notes

(1) Research sponsored by the Division of Basic Energy Sciences of the Department of Energy under contract with the Union Carbide Corporation.
(2) I. G. C. Dryden in "Chemistry of Coal Utilization", Suppl. Vol. 1, H. H. Lowry, Ed., Wiley, New York, N.Y., 1963, Chapter 6.
(3) D. W. Van Krevelin, "Coal", Elsevier, New York, N.Y., 1961, Chapter 9.
(4) Reference 2, p 276; E. R. Altwickel, *Chem. Rev.*, **67**, 475 (1967).
(5) H. Musso in "Oxidative Coupling of Phenols", W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N.Y., 1967, Chapter 1.
(6) Reference 2, p 272; G. R. Yohe, D. R. Hill, J. E. Dunbar, and F. M. Sheidt, *J. Am. Chem. Soc.*, **75**, 2688 (1953).
(7) The acids isolated from the oxidation of coal by our method will be reported elsewhere. The oxidation procedure was conceived by V. F. Raaen. BHT is a common antioxidant and also has been found in brown coals.
(8) S. J. Hurst and J. M. Bruce, *J. Chem. Soc.*, 1321 (1963).
(9) S. Brownstein and K. I. Ingold, *J. Am. Chem. Soc.*, **84**, 2258 (1962).
(10) R. Magnusson, *Acta Chem. Scand.*, **20**, 2211 (1966).
(11) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).
(12) J. Sugita, *Nippon Kagaku Zasshi*, **87**, 1082 (1966); A. Ronlán, *Chem. Commun.*, 1643 (1971).
(13) A. Nishinego, T. Itahara, and T. Matsuura, *Chem. Lett.*, 667 (1974).
(14) G. R. Yohe, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, *J. Org. Chem.*, **21**, 1289 (1956).
(15) D. Lauer, E. L. Motell, D. D. Traficante, and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 5335 (1972).
(16) E. Wenkert, M. J. Gasić, E. W. Hagaman, and L. D. Kwart, *Org. Magn. Reson.*, **7**, 51 (1975).
(17) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(18) X-ray structure determination of **5** was done by P. Rafferty, B. M. Benjamin, V. F. Raaen, W. E. Thiessen, and C. K. Johnson, Chemistry Division, Oak Ridge National Laboratory, and will be published separately. In the crystalline state, **5** exists in the boat conformation and all the oxygen atoms are on the same side of the molecule.
(19) G. M. Brown, to be published separately.
(20) J. D. Roberts, F. J. Weigert, J. K. Kroschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).
(21) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1347 (1970).
(22) W. A. Waters, *J. Chem. Soc. B*, 2026 (1971).

Carbon Monoxide–Hydrogen–Water: Reduction of Anthracene, Dihydroanthracene, and Quinoline

V. I. Stenberg,* J. Wang, R. J. Baltisberger, R. Van Buren, and N. F. Woolsey

Department of Chemistry, The University of North Dakota, Grand Forks, North Dakota 58202

J. E. Schiller and D. J. Miller

Grand Forks Energy Research Center, Grand Forks, North Dakota 58201

Received September 5, 1977

Anthracene is reduced by $CO–H_2O$, $CO–H_2O–H_2$, or H_2 at 425 °C and an initial pressure of 1500 psi to dihydroanthracene, 1,2,3,4-tetrahydroanthracene, and methylbenzohydrindene. Hydrocracked products and dimers are formed to a minor extent. The hydrogen donor solvent, tetralin, promotes rearrangement and cracking. Tetralin also increases the formation of methylbenzohydrindene, but does not influence the overall conversion. Ferrous sulfide promotes rearrangement and cracking while lowering the overall conversion. Sodium carbonate retards the reaction. Dihydroanthracene disproportionates to anthracene and tetrahydroanthracene under the reaction conditions. The principal reduction product of quinoline under similar conditions is 1,2,3,4-tetrahydroquinoline. Fragmented aniline derivatives, dimeric quinoline species, and methylated compounds are also found in the reaction mixture. Hydrogen is most effective as a reducing gas, and carbon monoxide must have water present to accomplish the reduction. Iron sulfide and sodium carbonate promote the carbon monoxide reductions.

Carbon monoxide is a versatile feedstock in that it can be used to synthesize a variety of chemicals such as sodium formate, methanol, ketones, adipic acid, aldehydes, ethylene glycol, glycidic acids, and hydrocarbons. This is in spite of the fact that it contains the strongest covalent bond known which exceeds that of nitrogen gas by 30 kcal/mol[1,2] and acetylene by 27 kcal/mol.[3,4] Carbon monoxide is now recognized as a superior reducing agent for the liquefaction of lignite[4–7] and other materials.[8,9] With benzophenone, there is evidence that it reacts via the formate ion in basic solutions.[8]

Anthracene reduction has been studied using hydrogen and hydrocracking catalysts.[10–14] Blom et al.[13] have reported dihydroanthracene and tetrahydroanthracene are formed under more mild hydrogenation conditions. As the conditions become more severe, isomerization to substituted indane and hydrocracking to naphthalene and benzene derivatives occur.

Since pyridine is more readily reduced than benzene,[15] it is not surprising that the pyridine portion of quinoline is selectively saturated. However, in acid media, the benzo group of quinoline can be selectively reduced.[16] Hydrogenation to decahydroquinoline is difficult.[17] Ring rupture to give 3-methylindole, *N*-methyl-*o*-toluidine, and *o*-toluidine occurred when quinoline was reduced over nickel in the vapor phase at 260–380 °C.[16] Catalytic hydrogenation of quinoline can also give alkylated anilines.[18]

Carbon monoxide can alkylate molecules also. Under Fischer-Tropsch-like conditions, a synthesis gas mixture of carbon monoxide, nitrogen, and hydrogen containing piperidine gave C_{1-8}-alkylpiperidines.[19]

The study herein described utilizes three sets of reducing gases with and without potential catalysts to reduce quinoline and anthracene, models for portions of the lignite structure. Quinoline assumes additional importance in model compound studies in relation to denitrification processes so important to coal conversion studies.

Experimental Section

Batch Autoclave Reductions. All the reductions were done in two 250-mL Hastelloy alloy C batch autoclaves (Autoclave Engineers, Inc.) using a heater designed to accommodate both autoclaves simultaneously and mixing achieved by rocking. Each autoclave contained, when specified, a catalyst, solvent, water, and reducing gases. The time of each run was 2 h at 425 °C not including heat-up and cool-down times. The initial charging pressure at room temperature was 1500 psi.

After the autoclaves were cooled and decompressed, the organic

0022-3263/78/1943-2991$01.00/0