conditions for oxychlorination were as follows: $HCl/C_2H_4/C_2D_4/$air = 2.5/1/2.5; temperature 490–505°; contact time = 7.0 sec at 500°. The products (per cent yield based on total ethylene) were CO (9.7); CO_2 (2.4); VCl (61.8); 1,1-dichloroethylene (3.2); CCl_4 (0.8); *trans*-1,2-dichloroethylene (4.8); *cis*-1,2-dichloroethylene (4.8); DCE (9.7); 1,1,2-trichloroethylene (0.8); 1,1,2-trichloroethane (2.4); other samples ±6% these results; conversion (C_2H_4 + C_2D_4) 50.7%; carbon balance 90.1%.

Registry No.—C_2D_4, 683-73-8; C_2H_4, 74-85-1.

Acknowledgments.—We want to thank A. E. Sir Louis and G. L. Chonko for technical assistance. We also want to thank Dr. P. Zakriski, P. Lightner, and B. Boose for performing and interpreting the mass spectra. Also we wish to thank Professor P. D. Bartlett for helpful discussions.

Selective Autoxidation of Some Phenols Using Bis(salicylaldehyde)ethylenediiminecobalt Catalysts

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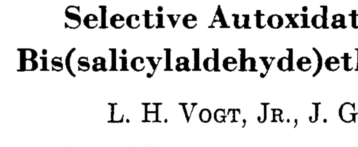
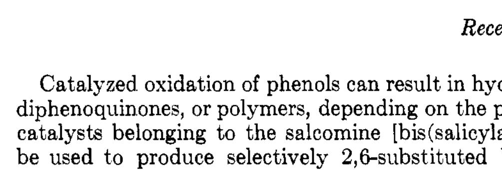
Catalyzed oxidation of phenols can result in hydroxylations, Diels–Alder coupling, aminations, benzoquinones, diphenoquinones, or polymers, depending on the particular catalyst system employed. We have found that two catalysts belonging to the salcomine [bis(salicylaldehyde)ethylenediiminecobalt (II)] family of complexes can be used to produce selectively 2,6-substituted benzoquinones, 3,3′,5,5′-tetrasubstituted diphenoquinones, or 2,6-substituted phenylene oxide polymers from several 2,6-substituted phenols. Conditions favoring the benzoquinone formation employ the salcomine monopyridine catalyst in high concentration and low temperature whereas the diphenoquinone is favored using the O_2-bridged salcomine dimer in low concentration and at high temperature. 2,6-Phenylene oxide polymers form when an amine is added to the system catalyzed by the O_2-bridged salcomine dimer. Evidence is presented for an equilibrium between a mononuclear salcomine and its O_2-bridged dimer. Selectivity of the catalysts may be associated with this equilibrium.

The catalyzed autoxidation of phenols is interesting both in mechanistic studies and in various syntheses.[1,2] Tetraalkyldiphenoquinones (eq 1), polyphenylene ethers (eq 2), and *o*-benzoquinones (eq 3) can be selectively prepared by proper choice of catalyst, solvent, and phenol.[3-6]



(1)



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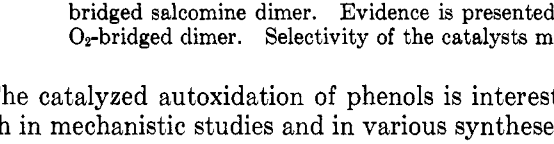

(3)

It is probable that the only function of oxygen in any of these reactions is to reoxidize copper from the 1+ to the 2+ state.[7,8] The suggestion that phenoxyl radicals are intermediates fails to account for the dramatic effects that result when the ligands on the copper catalyst are changed.

Recent work by van Dort and Geursen[9] and workers at Dynamit Nobel[10] has shown that copper is not the only metal that can be used in these reactions. Cobalt, as a salcomine,[11] produces all three classes of products (eq 4).

A similar reaction in chloroform gave a 26% yield of benzoquinone, an 11% yield of polymer, and no detectable diphenoquinone. It is curious that in contrast to the copper catalyst,[6] the cobalt catalyst produced little or no *o*-benzoquinone even with phenols having open 2 positions.

Although 13 other examples are given, only 2,6-diphenylphenol gave all three products. In the other cases, the benzoquinones were often the only identified product in yields ranging from 80% for 2,6-di-*t*-butylphenol to 36% with 2,3-dimethylphenol.

Until recently, nearly all of the interest in salcomines has been in the area of physical chemistry with surprisingly little emphasis on their chemical reactions, even though it has been known for about 25 years that certain salcomines can combine reversibly with molec-

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[1] J. L. Bolland and P. ten Have, *Discussions Faraday Soc.*, **2**, 252 (1948); C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Amer. Chem. Soc.*, **77**, 3233, 3238, 3380 (1955).

[2] C. D. Cook, *J. Org. Chem.*, **18**, 260 (1953); E. Muller, A. Schick, R. Mayer, and K. Scheffler, *Ber.*, **93**, 2649 (1960); D. A. Bolon, *J. Amer. Chem. Soc.*, **88**, 3148 (1966); H. S. Blanchard, *J. Org. Chem.*, **25**, 264 (1960).

[3] A. S. Hay, U. S. Patent 3,210,384 (1965); *Chem. Abstr.*, **64**, 17494*b* (1966).

[4] A. S. Hay, *Advan. Polym. Sci.*, **4**, 496 (1967); G. F. Endres and J. Kwiatek, *J. Polym. Sci.*, **58**, 593 (1962).

[5] A. Rieche, B. Elschner, and M. Landbeck, *Angew. Chem.*, **72**, 385 (1960); H. Musso, *Angew. Chem. Intern. Ed. Engl.*, **2**, 723 (1963); W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," Methuen Ltd., London, 1964.

[6] W. Brackman and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **74**, 937 (1955).

[7] H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

[8] H. S. Blanchard, H. Finkbeiner, and G. F. Endres, *Soc. Plastics Eng. Trans.*, **2**, 110 (1962).

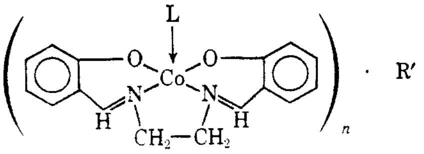
[9] H. M. van Dort, and H. J. Geursen, *Rec. Trav. Chim. Pays-Bas*, **86**, 520 (1967).

[10] Dynamit Nobel Aktiengesellschaft, Dutch Patent 6,609,843 (1967).

[11] The generic term salcomine has been applied to Schiff base coordination compounds consisting of salicylaldehyde, cobalt, and an amine. Salcomine (salco) is bis(salicylaldehyde)ethylenediiminecobalt(II). The bissalicylaldehyde Schiff base ligand is abbreviated as salen.

TABLE I

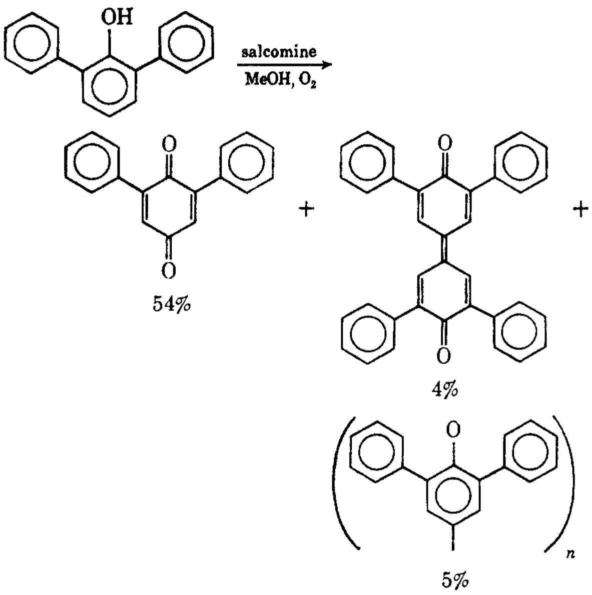
BIS(SALICYLALDEHYDE)ETHYLENEDIIMINECOBALT COMPLEXES



No.	n	Name	L	R′	Description	Ref
I	1	Salcomine (salco)	None	None	Red-brown crystals stable under vacuum or N_2; reacts at room temperature with O_2 to give (III) ($C_{16}H_{14}CoN_2O_2$; mol wt, 325.26)	12, *a*
II	1	Pyr–salco	Pyr	None	Red crystals stable in air; pyridine can be displaced thermally to give I; forms IV reversibly when exposed to O_2 in $CHCl_3$ solution ($C_{21}H_{19}CoN_3O_2$; mol wt, 404.33)	12, *a*
III	2	O_2–(salco)$_2$	None	O_2	O_2-bridged dimer; jet black crystals prepared from I plus O_2; O_2 can be displaced thermally to give I ($C_{32}H_{28}Co_2N_4O_6$; mol wt, 682.45)	12, *a*
IV	2	O_2–(salco-pyr)$_2$	Pyr	O_2	Brown solid, poorly characterized; soluble in $CHCl_3$ ($C_{42}H_{38}Co_2N_6O_6$; mol wt, 840.66)	*a*

[a] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1886 (1947); II was prepared as described on p 1887; III was obtained from II by heating at 160° (10^{-4} mm) for 2 hr.

ular oxygen.[12] However, not one bis(salicylaldehyde)ethylenediimine complex containing a metal other than cobalt has been found to be a reversible oxygen carrier.



(4)

Table I gives some of the pertinent data that characterize the four compounds of interest. Hereafter, Roman numerals I–IV refer to the specific salcomine designated in Table I.

In the work of van Dort and Geursen,[9] it is not clear which catalyst was used (the formula given for their catalyst is I, but the reference cited for the method of preparation[13] is for an alleged aquo dimer of I).

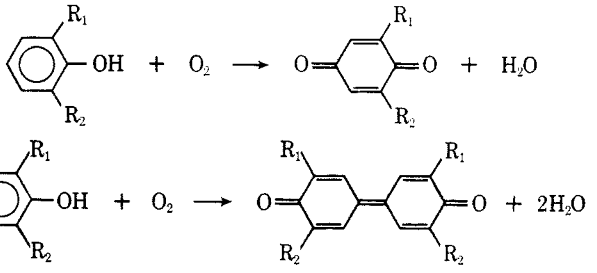
A number of questions arise concerning the behavior of the salcomines as catalysts in the oxidation of 2,6-substituted phenols, *viz.*, (1) do II and III lead to different products or product ratios; (2) what effect do concentration, temperature, solvent, etc., have on the oxidation; (3) do nonoxygen carrying bis(salicylaldehyde)ethylenediimine complexes containing metals like Fe, Mn, Cu, etc., show catalytic activity; and (4) can other reversible oxygen carriers such as Vaska's $Ir(CO)Cl[C_6H_5)_3P]_2$[14] complex catalyze phenol oxidations.

In order to answer these questions, a series of oxidations was carried out in which phenol, catalyst, solvent, temperature, catalyst concentration, and concentration of added amine were varied.

Results and Discussion

The only metal complexes that exhibited appreciable catalytic activity (50% or more of 2,6-dimethylphenol oxidized in 24 hr) were the cobalt complexes. Under the conditions described (Experimental Section), Cu^{II} (salen), Fe^{II} (salen), Mn^{II} (salen), Ni^{II} (salen), and $Ir^{I}(CO)[(C_6H_5)_3P]_2X$ (where X = Cl, Br, I) were all inactive as indicated by recovery of essentially all of the 2,6-dimethylphenol after 24 hr. About 10% of the phenol was oxidized by $V^{IV}O$ (salen) in the same time suggesting that the vanadium complex was acting stoichiometrically rather than catalytically.

The products of the oxidation of the 2,6-substituted phenols shown in Table II are predominantly the corresponding 2,6-disubstituted benzoquinones (BQ) or 3,3′,5,5′-diphenoquinones (DPQ).



Benzoquinone formation is not common in metal-catalyzed oxidations of phenols. For example, in the oxidation of 2,6-dimethylphenol with a copper catalyst (methanol green),[7] the DPQ is formed in the total absence of the BQ[15] (Table II, expt 17) although the same catalyst does give both BQ and DPQ when 2-methyl-6-benzylphenol is oxidized (expt 16). In general, for the same concentration of both salcomine catalysts (based on the gram-atoms of cobalt present), the pyr–salco catalyst gave higher BP/DPQ ratios for all of the phenols oxidized than the O_2-(salco)$_2$ catalyst, *e.g.*, expt 10, 22, 26, and 8 compared to 4, 21, 25, and 27, respectively. The BQ/DPQ ratio can be altered

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(12) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963); A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice Hall, Englewood Cliffs, N. J., 1954, pp 337–352.

(13) H. Diehl and C. C. Hach, *Inorg. Syn.*, **3**, 196 (1950).

(14) L. Vaska, *Science*, **140**, 809 (1963).

(15) G. F. Endres and H. Finkbeiner, unpublished results.

TABLE II

PRODUCTS OF THE CATALYTIC OXIDATION OF 2,6-SUBSTITUTED PHENOLS[b]

Expt no.	2,6-Phenol	Temp, °C	Solvent	Catalyst	Catalyst concn[a]	Conversion,[k] %	Amt, %[c]		BQ/DPQ
							Benzo	Dipheno	
1	Me, Bz (benzyl)	50	$CHCl_3$	O_2–(salco)$_2$	10:1	100	26.9	57.6	0.47
2	Me, Bz	20	$CHCl_3$	O_2–(salco)$_2$	10:1	89	66.9	16.6	4.03
3	Me, Bz	20	$CHCl_3$	Diehl[d]	10:1	89	82.0	24.0	3.42
4	Me, Bz	20	$CHCl_3$	O_2–(salco)$_2$	20:1	73	58.1	41.9	1.39
5	Me, Bz	20	1.7$CHCl_3$[e]	O_2–(salco)$_2$	20:1	75	58.1	44.1	1.32
6	Me, Bz	20	$CHCl_3$–$MgSO_4$[f]	O_2–(salco)$_2$	20:1	70	63.6	40.6	1.57
7	Me, Bz	50	$CHCl_3$	Pyr–salco	10:1	76	63.5	25.6	2.48
8	Me, Bz	20	$CHCl_3$	Pyr–salco	10:1	71	73.3	9.3	7.88
9	Me, Bz	20	$CHCl_3$–H_2O[g]	Pyr–salco	20:1	71	79.3	8.6	9.24
10	Me, Bz	20	$CHCl_3$	Pyr–salco	20:1	59	76.8	22.0	3.50
11	Me, Bz	20	$CHCl_3$–$MgSO_4$[f]	Pyr–salco	20:1	64	72.6	12.7	5.72
12	Me, Bz	20	$CHCl_3$–$NaSO_4$[f]	Pyr–salco	20:1	62	73.7	14.6	5.05
13	Me, Bz	20	C_6H_6	Pyr–salco	20:1	67	84.8	3.9	21.7
14	Me, Bz	20	C_6H_6	O_2–(salco)$_2$	20:1	26	37.6	57.8	0.65
15	Me, Bz	20	CH_3OH	O_2–(salco)$_2$	20:1	86	43.3[j]	14.9[j]	2.91
16	Me, Bz	20	$CHCl_3$	Methanol green[h]	20:1	49	19.4	63.0	0.31
17	Me, Me	20	$CHCl_3$	Methanol green[h]	20:1	68	0.0	69.2[l]	0.00
18	Me, Me	20	$CHCl_3$	Salcomine[i]	20:1	93	56.0	53.7	1.04
19	Me, Me	20	$CHCl_3$	Diehl[d]	20:1	92	59.8	53.4	1.12
20	Me, Me	20	$CHCl_3$	O_2–(salco)$_2$	10:1	96	69.4	29.9	2.32
21	Me, Me	20	$CHCl_3$	O_2–(salco)$_2$	20:1	85	51.5	43.7	1.18
22	Me, Me	20	$CHCl_3$	Pyr–salco	20:1	78	81.4	22.5	3.62
23	Me, Me	20	$CHCl_3$	Pyr–salco	10:1	88	88.6	11.1	7.97
24	Me, Me	20	$CHCl_3$	O_2–(salco)$_2$	44:1	89	46.3	52.7	0.88
25	C_6H_5, C_6H_5	20	$CHCl_3$	O_2–(salco)$_2$	20:1	48	43.8	1.3	3.4
26	C_6H_5, C_6H_5	20	$CHCl_3$	Pyr–salco	20:1	48	39.6	0	
27	Me, C_6H_5	20	$CHCl_3$	O_2–(salco)$_2$	20:1	47	46.2	26.6	2.1
28	Me, C_6H_5	20	$CHCl_3$	Pyr–salco	20:1	38	85.6	17.3	4.95
29	Cl, Cl	20	$CHCl_3$	Pyr–salco or	20:1		No reaction		
30	H, H	20	$CHCl_3$	O_2–(salco)$_2$	20:1		No reaction		

[a] Moles of phenol/gram-atoms of metal in the catalyst. [b] The oxidations were stopped when the rate of O_2 absorption dropped to 0.01 ml/min. In most instances, this occurred about 700 min after the start of the oxidation. [c] Based on per cent conversion. Unless otherwise noted, only the unreacted phenols, BQ and DPQ, were detected. This does not preclude formation of somewhat higher molecular weight products that would not be detectable by glpc or tlc methods. However, the reaction mixture did not give a precipitate in CH_3OH indicating that high polymer ($[\eta] \gg 0.06$ dl/g) was not present. [d] Although the method used to make this complex alleges to give an aquo-bridged binuclear salcomine complex (see discussion), we assumed the product to be salcomine (I) itself, mol wt 325.26. [e] Used 1.7 times the standard volume (75 ml) of $CHCl_3$. [f] Drying agent (1 g, anhydrous $MgSO_4$ or Na_2SO_4) was added before the phenol was introduced. [g] Water (2 ml) was added before the phenol was introduced. [h] Methanol green is Cu(OCH_3)(Cl)(pyr); see Experimental Section. [i] Active salcomine (I) was stored in N_2 and was weighed out rapidly to avoid O_2 absorption. [j] The remaining 42% is unidentified products, probably resulting from the oxidation of the CH_3OH solvent by the catalyst. [k] The difference between this value and 100 is the per cent of the recovered, unreacted phenol. [l] In addition, a mixture (19%) of the corresponding dimer and trimer was recovered.

by changing solvent, catalyst concentration (Figure 1), and temperature (Table II).

Inspection of Table II shows that high BP/DPQ ratios (BQ the major product) are favored by the pyr–salco catalyst in high concentration (Figure 1) in a nonpolar solvent (expt 13 *vs.* 10) and at low temperatures (expt 8 *vs.* 7). Low BQ/DPQ ratios (DPQ the major product) are obtained for the O_2–(salco)$_2$ catalyst in low concentration, at high temperatures and in a nonpolar solvent (expt 14 *vs.* 4). Changing the solvent volume by a factor of 1.7 (expt 5 *vs.* 4) made no significant change. Thus by suitable manipulation of these variables, the oxidation can be directed to give high yields of benzoquinone (expt 13) or diphenoquinone (expt 1, 14).

The effect of water on the reaction is not understood. Both the addition of water (expt 9) and drying agents (expt 11, 12) increased the BQ/DPQ ratios for 2-methyl-6-benzylphenol over the values obtained when neither was added (expt 10). Since the amount of water produced by the oxidations should be about the same for all of the phenols investigated (and is in solution), drying agents were not employed routinely in our studies.

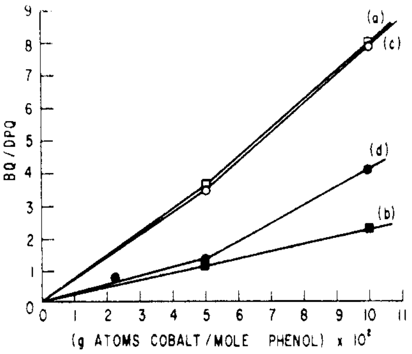
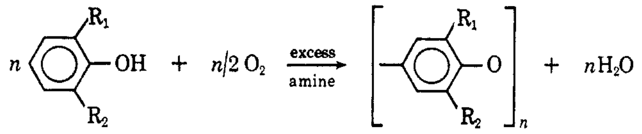


Figure 1.—A plot of BQ/DPQ *vs.* catalyst concentration for the oxidation of 2,6-dimethylphenol with (a) pyr–salco and (b) O_2–(salco)$_2$ and 2-methyl-6-benzylphenol with (c) pyr–salco and (d) O_2–(salco)$_2$. Reaction conditions are indicated in Table II: expt no. 23 and 24 for a, 20 and 21 for b, 8 and 10 for c, and 2 and 4 for d.

If N,N,N′,N′-tetramethylethylenediamine is added to any of the O_2–(salco)$_2$-catalyzed reaction mixtures shown in Table II (except those containing dichlorophenol or phenol), a low molecular weight phenylene oxide polymer ($[\eta]$ = 0.06 dl/g) is formed. In pyr–salco-catalyzed oxidations, polymer formation was not detected. Other workers[10] have reported that low molecular weight polymers can be obtained by salcomine-catalyzed oxidation of substituted phenols containing 5 mol % of the corresponding sodium phenoxide in lieu of an amine.



The rate of oxygen absorption was always slower initially for the O_2–(salco)$_2$ catalyst than for the pyr–salco catalyst. However, the rates of oxygen absorption became approximately the same after about 50% of the stoichiometric amount had reacted (based on a 1:1 molar ratio of phenol to O_2). A typical set of rate curves for the oxidation of 2-methyl-6-benzylphenol is shown in Figure 2. These rate curves are difficult to interpret since the stoichiometry requires 1 mol of oxygen/mol of phenol for benzoquinone formation and 0.5 mol/mol of phenol for diphenoquinone formation. Table III gives the volumes of O_2 absorbed in a period of 100 min for several phenols. The rate of oxygen absorption at 50° was slower for both catalysts than the rate at 20°. Similar temperature effects have been observed for the oxidation of 2,6-dimethylphenol using the methanol green catalyst.[7,15] The BQ/DPQ ratio did not change markedly during the course of the reaction (see Table IV).

Table III

O_2 Absorbed 100 Min after Initiation of Phenol Oxidations

Phenol	Volume of O_2 absorbed[a]	
	Pyr–salco	O_2–(salco)$_2$
2-Methyl-6-benzyl	81	55
2,6-Dimethyl	123	40
2-Methyl-6-phenyl	68	6
2,6-Diphenyl	42	12

[a] Stoichiometric O_2 for only DPQ formed is 120 ml and for only BQ formed, 240 ml.

Table IV

Changes in the BQ/DPQ Ratio during the Oxidation of 2-Methyl-6-Benzylphenol[a]

Minutes (days) from start of oxidation	Conversion, %	Amt, %		BQ/ DPQ
		BQ	DPQ	
5	27	52.9	19.5	2.7
20	27	57.5	19.2	3.0
50	44	64.9	21.3	3.3
80	66	69.6	17.2	4.1
400	91	69.8	16.8	4.2
(7)	94	65.1	19.6	3.3[b]

[a] Reaction conditions: temp 20°, $CHCl_3$ solvent, O_2–(salen)$_2$ catalyst, 10:1 catalyst concentration (moles of phenol/gram-atoms of cobalt). [b] The decrease in this ratio is due to loss of BQ on standing rather than an increase in DPQ.

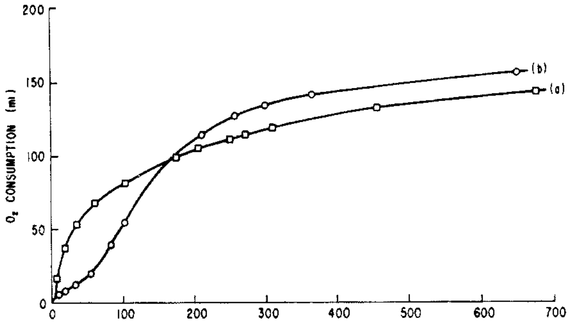


Figure 2.—Rate curves for oxidation of 2-methyl-6-benzylphenol catalyzed by (a) pyr–salco and (b) O_2–(salco)$_2$ complexes. Reaction conditions are indicated in Table II, expt no. 4 and 10.

These results along with those of van Dort and Geursen[9] show that salcomines are synthetically useful catalysts for the synthesis of *p*-benzoquinones and diphenoquinones and that copper catalysts are far superior for forming polyphenylene oxide polymers.

It is difficult even to attempt to draw analogies between the salcomine-catalyzed oxidations and the more extensively studied phenol oxidations which use organic peroxides. Different organic peroxides have been reported to give different BQ/DPQ ratios. Furthermore, the DPQ produced in some of these oxidations has frequently been reported in the "other products" category and was not determined quantitatively. Therefore, it is impossible to determine if the O_2 in O_2–(salco)$_2$ or O_2–(pyr–salco)$_2$ complexes is behaving like a "typical" peroxide oxygen. It is unlikely that the O_2 in these complexes is the only governing factor in the oxidations since the Vaska complexes are not oxidation catalysts even though the coordinated O_2 ligands vary in character (based on the O–O bond distance) from a superoxide (chloro complex) to a peroxide (iodo complex).

In solution, the apparent molecular weights of salcomines II and III show a dependence on concentration (Figure 3) indicating the existence of monomer–O_2-bridged dimer equilibria analogous to that reported for the salcomine in which R = γ,γ'-diaminodipropylamine.[16] These equilibria will also be affected by

$$O_2\text{–(pyr–salco)}_2 \rightleftharpoons 2\text{(pyr–salco)} + O_2$$

$$O_2\text{–(salco)}_2 \rightleftharpoons 2\text{(salco)} + O_2$$

changes in temperature and solvent. The quantities of DPQ and BQ appear to be correlated, respectively, with the amounts of mononuclear and O_2-bridged dimer present in the catalyst system (Figures 1 and 3). The hypothesis that mononuclear complexes give predominantly or exclusively DPQ and O_2-bridged dimer complexes BQ is currently being tested.

Experimental Section

I. **Reagents.**—2,6-Dimethylphenol was distilled before use. Reagent grade N,N,N',N'-tetramethylethylenediamine, chloroform, methanol, phenol, benzene, Aldrich 2,6-dichlorophenol and bis(trimethylsilyl)acetamide, and Eastman White Label diphenyl ether were used as received. It was shown that the small amount of ethanol present in reagent grade chloroform did not affect

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(16) H. P. Fritz and W. Gretner, *Inorg. Nucl. Chem. Lett.*, **3**, 14 (1967).

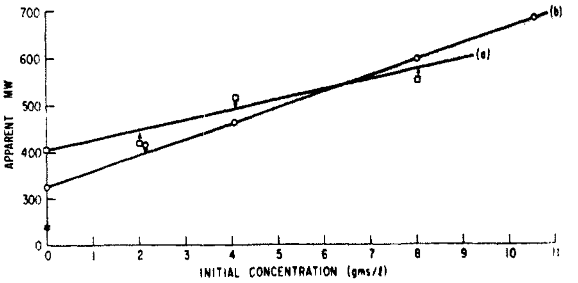

Figure 3.—Concentration *vs.* apparent molecular weight of (a) salco–pyr and (b) O_2–(salco)$_2$ in chloroform saturated with O_2. The abscissa gives the initial (not equilibrium) concentrations.

the reactions. Salcomine catalysts II and III were prepared by the method of Bailes and Calvin.[17] Methanol green [CuPyCl-(OCH_3)] was synthesized by Finkbeiner's method.[18] The following complexes were prepared by the method used for pyr–salco(II): [Cu^{II} (salen)],[19a] [Fe^{II}(salen)],[19b] [Mn^{II}(salen)],[19c] and [Ni^{II}(salen)].[19d] Billig and Bayer's[20] synthesis of [$V^{IV}O$-(salen)] was employed. Vaska's complexes—Ir(CO)[$(C_6H_5)_3P$]$_2$-X, where X = Cl, Br, I—were prepared by the following methods. For X = Cl,[21] 3 g of $IrCl_3 \cdot 3H_2O$ was made into a paste with 2 ml of water. Methylcarbitol (50 ml) was added followed by 20 g of triphenylphosphine. The reaction vessel was flushed with N_2 and heated to reflux. A reflux temperature of 190° was maintained by allowing water to boil off if the temperature was too low or by adding more water if it was too high. Reflux was continued for 3 hr after which the reaction mixture was cooled; the yellow crystals were filtered off, washed successively with methylcarbitol and petroleum ether, and dried at 60° under vacuum. A 75% yield (5 g) was obtained. The X = Br, I complexes were derived from the chloro complex by Halpern's method.[22] Literature methods are available for the preparation of 2-methyl-6-phenylphenol,[23] 2-methyl-6-benzylphenol,[24] and 2,6-diphenylphenol.[25]

II. Oxidations. A. Evaluation of Several Complexes as Oxidation Catalysts.—2,6-Dimethylphenol (1.22 g, 0.01 mol) was dissolved in 100 ml of $CHCl_3$ containing 0.005 mol of catalyst. Oxygen was bubbled through the solution for 24 hr, after which the reaction mixture was analyzed quantitatively for unreacted 2,6-dimethylphenol by glpc, and qualitatively for the oxidation products using analytical thin layer chromatography.

B. Oxidation of 2,6-Substituted Phenols.—Sufficient catalyst to contain 0.0005 g-atom of metal [*e.g.*, 0.00025 mol (0.170 g) of O_2–(salco)$_2$ or 0.0005 mol (0.202 g) of pyr–salco] was added to 75 ml of solvent (at 20 ± 2°). The reaction vessel was sealed under O_2 and vigorously stirred with a Vibromixer until the oxygen atmosphere was saturated with solvent vapor (about 0.5 hr). A solution of 0.01 mol of the phenol in 25 ml of solvent was added and the oxygen uptake was monitored. In all cases, after addition of the phenol, the solutions were homogeneous. After 12 hr, or when the rate of O_2 uptake was 0.01 ml/min, the reaction mixture was analyzed. At this stage, there are a few tenths of a gram of solid in the otherwise homogeneous system. The solid has a high Co content and is devoid of any phenol, benzoquinone, or diphenoquinone.

III. Analytical Methods.—The quantitative analysis of 2,6-dimethylphenol and its oxidation products was achieved by adding 0.340 g (2×10^{-5} mol) of diphenyl ether to the reaction mixture (as an internal standard) and diluting to 100 ml with $CHCl_3$. The benzo- and diphenoquinones were catalytically reduced with H_2 (50 mg of PtO_2) to the corresponding hydroquinones. Bis(trimethylsilyl)acetamide[26] (2 ml) was transferred to a 10-ml flask and diluted to the mark with the reduced reaction mixture. The resulting solution of silylated phenols was chromatographed [(F & M Model 700 gas–liquid partition chromatograph, 2 ft 10% silicone rubber UC-W98 column; temperature programmed 100–300° (10°/min)]. All of the components were well resolved and reproducible and quantitative data were obtained. If the reaction mixture were put through the glpc without first reducing and silylating, quantitative data could not be obtained since the benzo- and diphenoquinones decomposed.

All of the other phenols and their oxidation products were analyzed by preparative thin layer chromatography (Merck Preparative tlc–SiO_2 coated plates) using benzene as the eluent. The phenols and quinone bands were cut from the plates, extracted with acetone, and weighed. Both methods give results that are reproducible to about ±10% of the yields shown in Table II. Neither tlc nor glpc would necessarily detect higher molecular weight products than the diphenoquinone.

Eastman Kodak Type K301R chromatogram sheets (SiO_2 coated) were used for qualitative thin layer chromatography. Intrinsic viscosities were determined in $CHCl_3$ using a Ubbelohde viscometer.

IV. Polymerization.—The reaction conditions were identical with those described in part IIA of the Experimental Section except for the addition of 0.4 ml (0.004 mol) of N,N,N′,N′-tetramethylethylenediamine before the phenol was added. After 12 hr, the solution was poured into 1 l. of methanol containing 5 ml of acetic acid. The precipitated polymer was filtered and washed with methanol.

Registry No.—I, 14167-18-1; II, 18309-20-1; III, 18309-21-2; IV, 15878-97-4; 2-methyl-6-benzylphenol, 1208-45-3; 2-methyl-6-methylphenol, 576-26-1; 2-phenyl-6-phenylphenol, 2432-11-3; 2-methyl-6-phenylphenol, 17755-10-1.

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[17] See Table I, footnote *a*.

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[19] $Co(OAc)_2 \cdot 4H_2O$ was replaced by (a) $Cu(OAc)_2 \cdot H_2O$, (b) $FeCl_2 \cdot 4H_2O$, (c) $MnCl_2 \cdot 4H_2O$, (d) $Ni(OAc)_2 \cdot 4H_2O$.

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