analysis of the remainder of the product on a 5 ft × 0.125 in. column of 10% Carbowax 20M on 80–100 mesh (DMCS), A-W revealed small amounts (<5% total) of several other products.

Reaction of 1a with 2b.—A solution of **1a** (16.9 g, 0.07 mol) and freshly distilled **2b** (10.5 g, 0.15 mol) in 25 ml of dry benzene was stirred at reflux for 4 days under N_2. Petroleum ether (bp 40–60°) was added to the mixture at room temperature, causing a black oil to separate with a solid suspended in it. Distillation of the petroleum ether–benzene gave back 4.5 g (27%) of **1a**.

The black oil was redissolved in benzene and a small amount of solid precipitated was filtered from solution. Separation and subsequent purification identified the solid as diphenylphosphinic acid. The benzene solution was distilled to give 5.0 g (34.5%) of ethyl diphenylphosphinate (based on **1a**), identified by comparison with an authentic sample.[14]

Registry No.—**3**, 23646-70-0; **4**, 23596-01-2; **9**, 23646-71-1.

(14) A general procedure for the preparation of alkyl diarylphosphinates is available; see K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *J. Org. Chem.* **30**, 1267 (1965).

Autoxidation of Some Phenols Catalyzed by Ring-Substituted Salcomines

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It has been shown that salcomines (see Table I) catalyze the autoxidation of 2,6-substituted phenols selectively, to give the corresponding benzoquinones (BQ), diphenoquinones (DPQ), or polymers.[1] The selectivity of the salcomine catalysts was correlated, in a qualitative way, with the amounts of the mononuclear salcomine and its O_2-bridged dimer present in solution at equilibrium.

We studied the catalytic oxidation of 2-methyl-6-benzylphenol and 2,6-dichlorophenol using a series of ring-substituted salcomines to see whether the nature of the substituent would affect their selectivity or oxidizing power (the dichlorophenol cannot be oxidized with unsubstituted salcomines).[1] Several *stoichiometric* oxidations of 2-methyl-6-benzylphenol were carried out using the unsubstituted pyr-salcomine and varying the time at which O_2 was admitted to the system.

Experimental Section

Preparation and Properties.—The preparation and properties of all of the salcomines used in this study are described in the literature.[1-3] They are readily obtained in high purity as highly colored, crystalline solids by the reaction in aqueous solution of a cobalt salt, ethylenediamine, and pyridine with the appropriate substituted salicyaldehyde. The elemental analyses (C, H, N, Co, and halogen when present), color, and crystal form of all of the salcomines used in this study were in excellent agreement with those reported in the literature.

Oxidations. Salcomines in Catalytic Amounts.—To a mixture of 0.0005 mol of catalyst (based on the molecular weights shown in Table I) in 100 ml of chloroform was added 0.01 mol of the 2,6-substituted phenol. Oxygen was bubbled through the solutions at room temperature for 24 hr. The reaction mixtures were then filtered, diluted to 250 ml with chloroform, and analyzed as described below.

Salcomines in Stoichiometric Amounts.—The catalyst used in these oxidations was bis(salicylaldehyde)ethylenediiminepyridinecobalt(II) (Table I, entry 10), and the phenol used was 2-methyl-6-benzylphenol. Two procedures were followed.

(A) The catalyst (0.005 mol, 2.02 g) was slurried with 140 ml of $CHCl_3$ *under nitrogen*. Then 0.01 or 0.005 mol (1.98 or 0.99 g) of the phenol was added as a solution (flushed with N_2) in 130 ml of $CHCl_3$. The initial red-purple color of the slurry did not change during this time, or for 0.5 hr after the phenol was added. The heterogeneous mixture was then flushed with O_2 and within 5 sec it turned dark brown and became homogeneous. Oxygen was bubbled through the solution for a total of 24 hr, after which it was filtered, made up to 250 ml with $CHCl_3$, and analyzed as described below.

(B) The catalyst (0.005 mol, 2.02 g) was slurried with 140 ml of $CHCl_3$ *under oxygen*. The phenol (0.01 and 0.025 mol) was then added and procedure A was followed from this point on. The mixture was brownish before and after adding the phenol and became homogeneous after adding the phenol.

C. Analytical Methods.—The reaction mixtures were analyzed for products and unreacted 2,6-disubstituted phenols using methods described previously.[1]

A qualitative test for the presence of polymers was made by pipetting a few milliliters of the reaction mixture into 100 ml of methanol. The absence of a precipitate indicated that if any polymers were present they were of very low molecular weight ($[\eta] < ca.$ 0.01 dl/g).

The 2,6-dichlorobenzoquinone could not be isolated by tlc, since it appeared to react with itself on the tlc plates to give an insoluble product. It was necessary to reduce the reaction mixture with zinc–acetic acid, acetylate the corresponding hydroquinone using acetic anhydride, and identify the resulting product from its glpc retention time, mass spectrum, and ir spectrum by comparison with authentic material.

Results and Discussion

The results of the catalytic oxidations of 2-methyl-6-benzylphenol are shown in Table II. A general trend in the conversions and oxidation products was observed in progressing from the more electron-donating groups as substituents on the phenyl rings of the salcomine catalysts to the more electron-withdrawing groups. The donor group favored higher conversions, higher yields of the BQ, and lower yields of the DPQ than the withdrawing groups. A more precise correlation between the nature of the products and the relative strengths of the donating or withdrawing groups is not possible at this time. There were no apparent correlations of the BQ to DPQ ratios with Hammett σ values. If we consider our earlier suggestion[1] that BQ's arise from reaction of the phenols with the O_2–bridged salcomine dimers and DPQ's by reaction with their mononuclear forms (in an equilibrium mixture), then our present data suggest that electron-withdrawing groups shift the equilibrium to favor the mononuclear species and the electron-donating groups favor the binuclear species. This suggestion is supported by inspection of a plot of per cent oxygenation *vs.* O_2 pressure for the 3-methoxy- and 3-nitrosalcomines.[4] At atmospheric pressure the methoxy derivative is more highly oxygenated, *i.e.*, more of it is in the O_2-bridged dimer form, than the 3-nitro derivative.

We considered the possibility that the formation of a BQ or DPQ could be determined by the oxidation potential and/or coordination geometry of either a phenol–

(1) L. H. Vogt, Jr., J. G. Wirth, and H. L. Finkbeiner, *J. Org. Chem.*, **34**, 273 (1969).

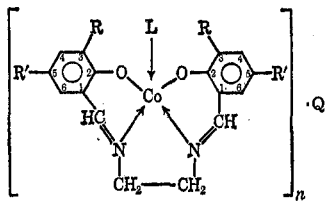
(2) R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1886 (1947).

(3) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.* **63**, 269 (1963).

(4) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, pp 346, 347.

TABLE I

DESCRIPTION OF THE CATALYSTS[a]



Name[b]	Registry no.	n	L	Q	R	R′	Color
Aquo-3-fluorosalcomine	23602-19-9	1	H_2O	None	F	H	Red
Pyr-3-fluorosalcomine	23602-20-2	1	Pyr	None	F	H	Red
O_2-(3-Fluorosalcomine)$_2$	23602-21-3	2	None	O_2	F	H	Black
Pyr-5-nitrosalcomine	23602-22-4	1	Pyr	None	H	NO_2	Red-brown
Pyr-3-nitrosalcomine	23602-23-5	1	Pyr	None	NO_2	H	Red-brown
Pyr-5-chlorosalcomine	23602-24-6	1	Pyr	None	H	Cl	Red-brown
Aquo-3-methoxysalcomine	18433-55-1	1	H_2O	None	OCH_3	H	Brown
Pyr-3-methoxysalcomine	23602-25-7	1	Pyr	None	OCH_3	H	Brown
O_2-(3-Methoxysalcomine)$_2$	23602-26-8	2	None	O_2	OCH_3	H	Black
Pyr-salcomine[c]	18309-20-1	1	Pyr	None	H	H	Red
O_2-Salcomine[c]	23602-28-0	2	None	O_2	H	H	Black

[a] Refer to Experimental Section for references to the preparation and characterization of the salcomines (ref 1–3). [b] The chemical names are abbreviated in the table. The complete names for these compounds are analogous to those given previously.[1] [c] Reference 1.

TABLE II

CATALYTIC OXIDATIONS OF 2-METHYL-6-BENZYLPHENOL

Catalyst	Conversion, %	BQ,[a] %	DPQ,[b] %	Ratio of BQ to DPQ
Aquo-3-fluorosalcomine[c]	66	52	61	1
Pyr-3-fluorosalcomine	39	76	29	3
Pyr-5-nitrosalcomine	20	50	21	2
Pyr-3-nitrosalcomine	7	47	53	1
Pyr-5-chlorosalcomine	53	54	42	1
Aquo-3-methoxysalcomine[c]	95	82	10	8
Pyr-3-methoxysalcomine	100	94	15	6
Pyr-salcomine	59	77	22	4

[a] 2-Methyl-6-benzylbenzoquinone. [b] 3,3′-Dimethyl-5,5′-dibenzyldiphenoquinone. [c] A duplicate experiment in which 0.4 ml (0.004 mol) of N,N,N′,N′-tetramethylethylenediamine (TMEDA) was added before adding the phenol did not result in the formation of polyphenylene ethers.

TABLE III

STOICHIOMETRIC OXIDATIONS OF 2-METHYL-6-BENZYLPHENOL[a]

Mole ratios of pyr-salcomine to phenol	O_2 Addition[b]	BQ,[c] %	DPQ,[c] %	Ratio of BQ to DPQ
2:1	After	88	19	5
2:1	Before	78	14	6
1:1	After	100	10	10
1:1	Before	95	10	10

[a] In all cases pyr-salcomine was used and 100% conversion of the phenol was obtained. [b] "After" indicates that O_2 was admitted to the system after the pyr-salcomine and phenol had been mixed–in $CHCl_3$ solution. "Before" indicates that the pyr-salcomine–$CHCl_3$ mixture had been saturated with O_2 before adding the phenol. [c] See Table II, footnotes *a* and *b*, for proper names.

TABLE IV

CATALYTIC OXIDATION OF 2,6-DICHLOROPHENOL

Catalyst	Conversion, %	Products[a]
Aquo-3-fluorosalcomine[b]	55	2,6-Dichlorobenzoquinone + X
Pyr-3-fluorosalcomine	18	2,6-Dichlorobenzoquinone
Pyr-5-nitrosalcomine	20	2,6-Dichlorobenzoquinone
Pyr-3-nitrosalcomine	20	2,6-Dichlorobenzoquinone
Pyr-5-chlorosalcomine	20	2,6-Dichlorobenzoquinone + X
Aquo-3-methoxysalcomine[b]	41	2,6-Dichlorobenzoquinone
O_2-(3-Methoxysalcomine)$_2$	32	2,6-Dichlorobenzoquinone
Pyr-salcomine	No reacn	2,6-Dichlorobenzoquinone

[a] "X" indicates that a second product (red-orange in color) was detected on tlc. It moved slower than the benzoquinone; its composition was not determined. "X" was 25% by weight of the products using the aquo-3-fluorosalcomine and 44% by weight using the pyr-5-chlorosalcomine. [b] TMEDA added as in Table II, footnote *c*.

salcomine complex or a phenol–salcomine-O_2 complex. Thus the presence or absence of O_2 during the initial stage of the reaction could be a critical reaction variable. This hypothesis was tested by running four stoichiometric oxidations in which the molar ratio of 2-methyl-6-benzylphenol to pyr-salcomine, and the stage at which O_2 was introduced, were varied. Table III shows that addition of the O_2 before or after the phenol was added to the salcomine did not significantly affect the amounts of the BQ or DPQ produced.

That the substituents can change the oxidation potential of the catalyst is clearly evidenced by the data shown in Table IV for the oxidation of 2,6-dichlorophenol (unsubstituted salcomines do not catalyze the oxidation of the dichlorophenol). Unfortunately, there is no correlation at all between salcomines containing donating or withdrawing groups and the degree of conversions or product distributions.

Polymers were not detected in any of the reaction mixtures, and the presence of TMEDA during the oxidation did not effect polymer formation (see Table II, footnote *c*, and Table IV, footnote *b*.

Registry No.—2-Methyl-6-benzylphenol, 1208-45-3; 2,6-dichlorophenol, 87-65-0.

Acknowledgments.—We appreciate the contributions of Dr. J. V. Crivello and Dr. H. L. Finkbeiner in suggesting several possible mechanisms and experiments to explain the bahavior of the catalysts. Dr. J. R. Ladd and M. Trier prepared most of the salcomine ring derivatives. Professor M. Calvin gave us some of the difficult-to-make 3-fluorosalicylaldehyde. A. M. Toothaker isolated the acetylated 2,6-dichlorohydroquinone. Elemental analyses were performed by the Analytical Chemistry Operation of the Research and Development Center.

Kinetics of Fischer–Hepp Rearrangement

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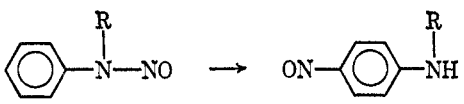
The rearrangement of aromatic nitrosamines on treatment with acids, particularly HCl and HBr, to give ring-substituted isomerides is known as the Fischer–Hepp rearrangement.[1] Although at one time



this reaction was believed to be truly intramolecular, considerable evidence accumulated in later years proved this to be untrue. Thus, when the rearrangement was carried out in the presence of urea, no C-nitroso isomeride was produced but only the secondary amine;[2] also, when the rearrangement occurs in the presence of more active foreign aromatic molecules, major transfers of the nitroso group to this molecule have been observed.[3,4] It has been found[3] that the conversion by HX occurs through the liberation of NOX, and with HCl and HBr the NO group is quantitatively removed. With sulfuric acid the yields are low, and with nitric acid no rearrangement occurs. The subsequent reaction of NOCl with the formed secondary amine to give C-nitroso compound was found to be very fast. To gain further insight into the mechanism of this reaction, a kinetic study seemed desirable, and the present work describes such a study on the hydrogen chloride catalyzed rearrangement of N-nitrosodiphenylamine to *p*-nitrosodiphenylamine.

Experimental Section

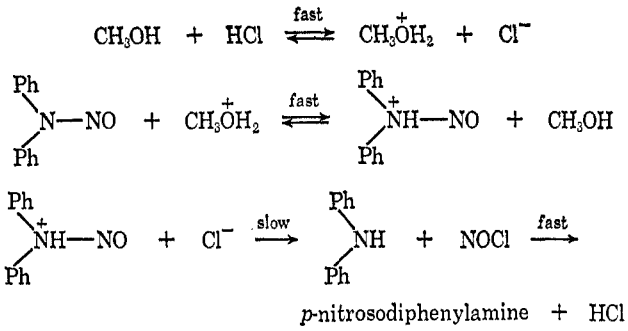
Eastman Kodak White Label compounds N-nitrosodiphenylamine and *p*-nitrosodiphenylamine were used. Analytical grade methanol and redistilled toluene were used as solvents. The solvent mixture was made up by volume. The stock solution of HCl (made by passing dry HCl into the solvent) in the desired solvent was variously diluted as required for the kinetic runs. The solution containing N-nitrosamine was mixed with the solution containing HCl in a volumetric flask thermostated at the desired temperature controlled within ±0.03°. Aliquots withdrawn at various times were quenched with methanolic sodium hydroxide, suitably diluted in methanol, and the absorbance at 430 mμ was measured in a 1-cm quartz cell on a Carl Zeiss (Models PMQ II and M4Q III) spectrophotometer to an accuracy of about 0.2%. The ultraviolet and visible spectra for both amines in methanol have been found to be similar to those reported in ethanol.[5] It has been established that the absorbance of *p*-nitrosodiphenylamine at this wavelength is linear with concentration (ϵ 16.74 × 10^3) in methanol in accordance with the Beer–Lambert law.

Results and Discussion

The rate of the reaction was found to be first order in nitrosamine and first order in hydrogen chloride at a given temperature and with a given solvent

$$\frac{-d[\text{N-nitrosamine}]}{dt} = \frac{d[\text{C-nitrosamine}]}{dt} = k_2[\text{N-nitrosamine}][\text{HCl}]$$

where k_2 is the second-order rate constant given in the last column of Table I. Arrhenius plots of log k against $1/T$ in the two solvents (not shown) are linear in the temperature range 30–50°, and the various activation parameters obtained from these plots are given in Table II.



A stepwise mechanism with a slow step involving the nucleophilic attack of chloride ion on the protonated N-nitrosamine requires third-order kinetics which are

$$\text{rate} = k_3[\text{N-nitrosamine}][\text{H}^+][\text{Cl}^-]$$

first order in each, nitrosamine, hydrogen ion, and chloride ion. Since the dependence of the rate on the concentration of chloride ion is indistinguishable from the stoichiometric concentration of molecular HCl, it seemed desirable to verify this mechanism by adding chloride ion. The results are shown in Table III where it can be seen that first-order dependence on chloride ion was not observed. The rate is still first

(1) O. Fischer and E. Hepp, *Ber.*, **19**, 2291 (1886).
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(3) P. W. Neber and H. Rauscher, *Ann.*, **550**, 182 (1942).
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