

to initial rates or to reactions in which one reagent is in considerable excess. The present nmr analysis therefore has uncovered complexities to this reaction that kinetic studies, based upon product analysis, could not hope to reveal.

### Experimental Section

**Preparation of Organomagnesium Compounds.**—Preparation and handling of the organomagnesium compounds was performed in a glass-to-glass sealed high vacuum apparatus as described previously.<sup>3</sup> Transfers were made *via* break-seal arrangements and samples were removed by sealing off side arms without use of stopcocks.

Neopentyl chloride, 100 mmol, was magnetically stirred with magnesium crystals,<sup>12</sup> 110 mg-atom, in 100 ml of tetrahydrofuran; no reaction took place during 4 days of continuous stirring although a cloud of powdered magnesium made the solution gray. On the addition of 6 mmol of 1,2-dichloroethane a slow reaction took place. The yield of neopentylmagnesium chloride was 85% after 7 days. The solution contained 5 mol % magnesium chloride and unreacted organic halides. After standing a few weeks a clear water-white solution was obtained which was freed from the sediment by decanting in the sealed vacuum system into another vessel and from which all volatile material was removed by cooling one arm of the apparatus with liquid nitrogen while gradually increasing the temperature in the other from 100 to 150° during a 5-hr period. New tetrahydrofuran was distilled onto the glassy residue. The nmr spectra of the solution, which was 0.85 *M* in RMgX and which contained 5 mol % magnesium chloride, showed that no unreacted halides were present. Small ampoules, *ca.* 2 ml, were filled with this solution for use in nmr work.

(12) The authors gratefully acknowledge the gift of sublimed magnesium from the Dow Chemical Co. It had the following maximum limits of elemental impurities in parts per million: Al, 1; Cu, 1; Fe, 4; Mn, 2; Ni, 4; Pb, 10; Si, 10; Zn, 100; Ba, 1; Ca, 18; K, 5; K, 5; Na, 6; Sn, 1.

On cooling of the neopentylmagnesium chloride solution in a carbon dioxide-acetone bath, beautiful crystals were obtained which contained mainly magnesium chloride. When the mother liquors were decanted and cooled anew, again crystals were formed which contained an excess of magnesium chloride over dineopentylmagnesium. This second mother liquor was again decanted from the crystals and found to contain 0.60 mmol of dineopentylmagnesium and 0.15 mmol of magnesium chloride/ml (total volume was 7 ml). To precipitate the total amount of 1.1 mmol of magnesium chloride 2.2 mmol of dioxane was added. After 3 weeks a solid white precipitate was formed from which the mother liquor (4.5 ml) was decanted; it contained 0.57 mmol of dineopentylmagnesium and 0.07 mmol of magnesium chloride/ml and was used without further purification.

**Nmr Measurements.**—Use was made of nmr tubes provided with a glass constriction to make sealing possible. Filling of the tubes was performed under high vacuum as usual and no special difficulties were encountered during such manipulations. Benzophenone was distilled from a side tube into the nmr tube containing the Grignard solution which was cooled to -80° (causing the formation of beautiful crystals). The distillation path was no longer than 10 cm and use was made of a "hot air gun" to control the distillation and solidification of the benzophenone on to the cooled glass wall above the THF solution. The tube was sealed, and the mixing of the reagents was done immediately before nmr measurements were started. In all cases reddish brown color appeared which changed to orange-yellow during the course of the reaction.

**Registry No.**—Neopentylmagnesium chloride, 13132-23-5; benzophenone, 119-61-9; magnesium bromide salt of diphenylneopentylcarbinol, 19978-29-1; diphenylneopentylcarbinol, 19978-30-4; dineopentylmagnesium, 19978-31-5.

**Acknowledgment.**—We thank Dr. Lois Durham for her cooperation and advice in collecting the nmr spectral data.

## The Oxidative Coupling of Phenols Using Vanadium Tetrachloride and Vanadium Oxytrichloride

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The oxidation of most simple phenols and some aniline derivatives with vanadium tetrachloride or vanadium oxytrichloride affords dimeric products which are coupled predominantly at the *para* position. For example, admixture of equimolar quantities of phenol and vanadium tetrachloride in an inert solvent followed by hydrolysis led to the isolation of 4,4'-diphenyl, 2,4'-diphenol, and 2,2'-diphenol in an approximate ratio of 8:4:1 and an over-all yield of 55-65%. The remainder of the product mixture was composed of unreacted phenol and <5% of chlorinated diphenols. Phenol itself was not oxidized by vanadium oxytrichloride, under the condition of vanadium tetrachloride oxidation; however, those phenol derivatives with lower oxidation potentials were coupled by this reagent. Thus, 1- and 2-naphthol reacted smoothly with vanadium oxytrichloride to produce 4,4'-dihydroxybinaphthyl and 2,2'-dihydroxybinaphthyl in 56 and 65% yields, respectively. The oxidative coupling reaction is believed to occur by a rearrangement of electrons in a complex containing at least two phenoxide (or phenol) residues and at least one metal center. Evidence in support of the existence of vanadium phenoxides has been obtained. The selectivity of the coupling reaction may be interpreted in terms of a polar or ionic transition state in which charges are developed in the aromatic ring.

The oxidative coupling of phenolic compounds has received considerable attention owing both to its utility as a synthetic reaction and its proposed involvement in the biosynthesis of a number of classes of natural products.<sup>1</sup> To date, the oxidation of the most of the simple phenols and naphthols has been studied with a variety of reagents and, in general, the products are complicated mixtures of dimeric, polymeric, and

quinonoid compounds.<sup>2</sup> In most cases, both carbon to carbon and carbon to oxygen coupling occurs, although, depending on the oxidant and on the experimental conditions, some selectivity can be attained.<sup>3</sup> We wish to report here results on two unique oxidizing agents, vanadium tetrachloride and vanadium oxytrichloride, which couple phenols and some aromatic amines predominantly at the *para* position and afford

(1) A recent survey of phenol oxidations is available: "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, Inc., New York, N. Y., 1967.

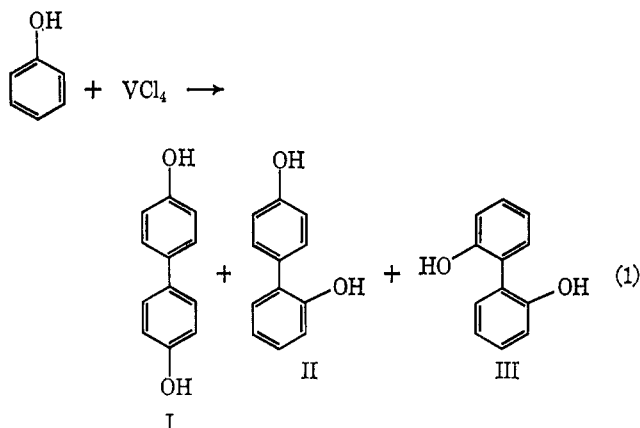
(2) Leading references can be found in H. Musso, ref 1, Chapter 1.

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

mainly dimeric products. These reagents grossly simplify the preparation 4,4'-diphenols and should find wide applicability throughout the area of phenolic oxidative coupling.

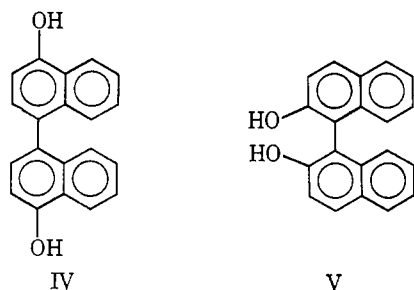
### Results

**Coupling of Phenols with Vanadium Tetrachloride.**—Admixture of equimolar quantities of phenol and vanadium tetrachloride in an inert solvent produced a black, finely dispersed precipitate with concomitant hydrogen chloride evolution. Hydrolysis of the reaction mixture and extraction led to the isolation of three products, identified as 4,4'-diphenol (I), 2,4'-diphenol (II), and 2,2'-diphenol (III) (eq 1) in an approximate ratio of 8:4:1 and an over-all yield of 55–65%. The



remainder of the product mixture was composed of unreacted phenol and <5% chlorinated biphenols. Products derived from carbon-oxygen coupling were never observed. In addition, a material balance study showed that the above products accounted for 96% of the initially charged phenol. Investigation of the aqueous layer indicated that vanadium(III) and -(IV) species were present; however, the relative amounts of both species was not determined.

The majority of the phenols which were treated with vanadium tetrachloride reacted (see Table I). Both 1- and 2-naphthols reacted cleanly to afford 4,4'-dihydroxybinaphthyl (IV) and 2,2'-dihydroxybinaphthyl (V) in 40 and 38% yields, respectively.



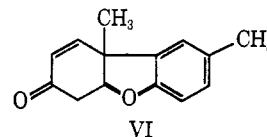
Reaction of the cresols with vanadium tetrachloride generally produced resinous materials from which dicresols could be isolated. For example, oxidation of *o*-cresol gave a 26% yield of 3,3'-dimethyl-4,4'-dihydroxybiphenyl and a deep blue material, possibly the quinhydrone of the above bisphenol and the corresponding diphenoquinone. Oxidation of *m*- and *p*-cresols yielded resinous mixtures from which only small quantities of 2,2'-dimethyl-4,4'-dihydroxybiphenyl and

TABLE I  
OXIDATION OF SUBSTITUTED AROMATICS WITH  
VANADIUM TETRACHLORIDE  
(substrate/VCl<sub>4</sub>, 1:1; 25°; CCl<sub>4</sub>)

Substrate	Product	Yield %
Phenol	4,4'-Dihydroxybiphenyl	34
	2,4'-Dihydroxybiphenyl	18
1-Naphthol	4,4'-Dihydroxybinaphthyl	40
2-Naphthol	2,2'-Dihydroxybinaphthyl	38
<i>p</i> -Cresol	2,2'-Dihydroxy-5,5'-dimethylbiphenyl	Small quantity
<i>m</i> -Cresol	2,2'-Dimethyl-4,4'-dihydroxybiphenyl	Small quantity
<i>o</i> -Cresol	3,3'-Dimethyl-4,4'-dihydroxybiphenyl	26
2,6-Xylenol	3,3',5,5'-Tetramethyl-4,4'-dihydroxybiphenyl	6
2,4,6-Tri-methylphenol	No reaction	
<i>o</i> -Chlorophenol	Unidentified products	Trace
N,N-Dimethylaniline	N,N,N,N-Tetramethylbenzidine	52
Diphenylamine	N,N-Diphenylbenzidine	43
Aniline	Aniline black (?)	Trace
Quinaldine	No reaction	
Anisole	No reaction	
Benzoic acid <sup>a</sup>	Trichloroacetophenone (?)	Trace
Ethyl benzoate	No reaction	

<sup>a</sup> At 65°.

2,2'-dihydroxy-5,5'-dimethylbiphenyl could be obtained. The resinous products from *p*-cresol also contained a small amount of "Pummerers ketone" (VI), a well-known oxidation product of *p*-cresol.<sup>4,5</sup> Vana-

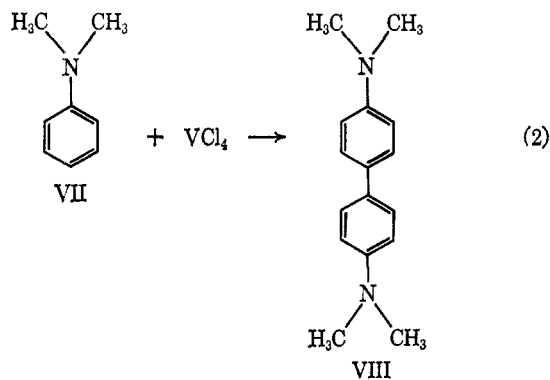


dium tetrachloride reacted with 2,6-xylenol to afford a 6% yield of 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl and an 18% yield of the corresponding quinhydrone. With 2,4,6-trimethylphenol, a vigorous evolution of hydrogen chloride occurred. However, on hydrolysis only the unreacted phenol was recovered. No oxidation products could be detected. When sodium phenoxide was used in place of phenol, chlorinated diphenols and other high boiling compounds were the major products.

Benzene, toluene, anisole, phenyl acetate, and ethyl benzoate all failed to react with vanadium tetrachloride under the standard conditions. Aniline and aniline derivatives were oxidatively coupled by vanadium tetrachloride. Thus, N,N-dimethylaniline (VII) afforded a 52% yield of N,N,N,N'-tetramethylbenzidine (VIII) (eq 2) and diphenylamine gave a 43% yield of N,N'-diphenylbenzidine. It is interesting to note that, in the case of N,N-dimethylaniline, smooth *para* coupling occurred in spite of the fact that the compound is a tertiary amine (in contrast with anisole, which does not react). Under the same conditions, aniline was oxidized to an unidentified black product, most probably "aniline black," whose infrared (ir) spectrum

(4) R. Pummerer, D. Melamed, and H. Puttfarcken, *Ber.*, **55**, 3116 (1922).

(5) K. Bowden and C. H. Pelce, *J. Chem. Soc.*, 2249 (1950).



showed *para* substitution. Reaction of 2-methylquinoline with vanadium tetrachloride failed to produce coupled products.

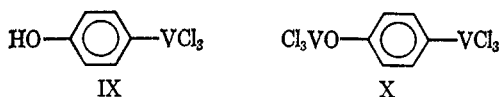
The yield of coupled products was found to be insensitive to the ratio of the reactants. Variations in the ratio of phenol to vanadium tetrachloride in the range of 4:1 to 1:4 failed to increase the yield of diphenol (Table II). The amount of hydrogen chloride liberated

TABLE II  
REACTION OF PHENOL WITH VANADIUM TETRACHLORIDE  
(25%; CCl<sub>4</sub>)

C <sub>6</sub> H <sub>5</sub> OH/VCl <sub>4</sub>	Yield of <i>p,p'</i> -diphenol <sup>a</sup>	HCl/VCl <sub>4</sub>	HCl/phenol
1	38	1.2	1.2
2	46	1.5	0.8
3	45	2.0	0.7
0.5	46	0.7	1.4

<sup>a</sup> Yields are based on the amount of the limiting reagent.

was, however, dependent on the ratio of phenol to vanadium tetrachloride (Table II). In all cases, more hydrogen chloride was evolved than could be accounted for solely on the basis of two molecules of hydrogen chloride being liberated per molecule of dimer produced. This indicates that vanadium to oxygen or vanadium to carbon bonds are also being formed with liberation of hydrogen chloride. To investigate the possibility that carbon to vanadium bonds such as in IX or X are formed, the mixture was hydrolyzed with deuterium oxide. The ir spectrum of the recovered



phenol did not show deuterium-carbon absorption, thus ruling out the presence of any substantial concentration of intermediates containing a carbon to vanadium bond at the time of hydrolysis.<sup>6</sup> The above facts show that the majority of the hydroxyl groups at the end of the reaction are tied up as vanadium phenoxides; however, this experiment does not exclude the intermediacy of vanadium-carbon bonds during the reaction.

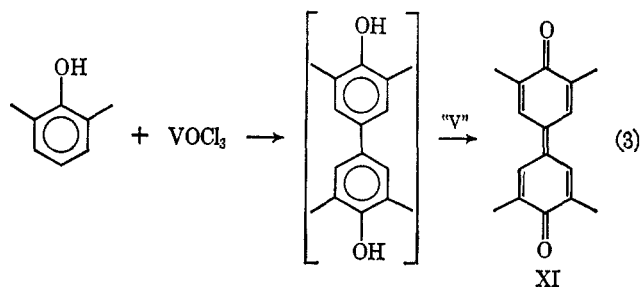
As reaction solvents, carbon tetrachloride, chloroform, chlorobenzene, benzene, and cyclohexane have all been employed. The solid complex formed in the reaction of phenol with vanadium tetrachloride is totally insoluble in these solvents. For example, filtration before hydrolysis of the product mixture (under

nitrogen) from reaction in carbon tetrachloride afforded a clear filtrate which was shown to be devoid of phenolic (phenol or diphenol) and vanadium(III) and -(IV) species. The elemental analysis of the precipitate was not consistent with any one structure, but suggested that the product was a complex mixture containing many components.

In control experiments, it was found that vanadium dichloride, vanadium trichloride, and hydrogen chloride do not interfere with the coupling reaction. However, both *o,o'*- and *p,p'*-diphenol react with vanadium tetrachloride and inhibit the phenolic oxidation reaction. Thus, addition of an equivalent amount of vanadium tetrachloride to a solution of *p,p'*-diphenol in chlorobenzene resulted in the liberation of hydrogen chloride and the formation of a black precipitate. Upon hydrolysis, the diphenol was recovered quantitatively. If 1 equiv of phenol is added to the above mixture before hydrolysis, little reaction takes place and 85% of the phenol is recovered unchanged. Attempts to increase the yield of coupled products by reoxidating the complexed vanadium(III) species with atmospheric oxygen, cupric chloride, stannic chloride, vanadium oxytrichloride, and other oxidizing agents were unsuccessful.

**Coupling of Phenols with Vanadium Oxytrichloride.**—Reaction of phenol with vanadium oxytrichloride under the conditions of the vanadium tetrachloride reaction resulted in the liberation of hydrogen chloride, but on hydrolysis phenol was completely recovered. When the reaction was carried out in refluxing chlorobenzene or refluxing phenol for extended periods of time, low yields of diphenol were obtained (<5%). The formation of diphenol, albeit in low yield, suggested that vanadium oxytrichloride may be a useful reagent for the oxidation of the more reactive phenols. Indeed, vanadium oxytrichloride reacted cleanly with 1- and 2-naphthols to produce 4,4'-dihydroxybinaphthyl (IV) and 2,2'-dihydroxybinaphthyl (V) in 56 and 65% yields, respectively (Table III). The course of the reaction was similar to the vanadium tetrachloride reaction in that hydrogen chloride was vigorously evolved and a dark precipitate was formed.

Oxidation of cresols with vanadium oxytrichloride gave a resinous material whose ir spectrum showed *para* substitution. Attempts to isolate bicresols from these materials were not successful. With 2,6-xyleneol, a 38% yield of 3,3', 5,5'-tetramethyl-4,4'-diphenylquinone (XI) was obtained (eq 3). In this case, no diphenol was isolated.



Vanadium oxytrichloride oxidized diphenylamine to an unidentifiable polymeric material. With *N,N*-dimethylaniline in an aqueous medium, a low yield of *N,N,N',N'*-tetramethylbenzidine was obtainable along

(6) It is possible that carbon-vanadium-bonded species do not hydrolyze to give carbon-hydrogen bonds: J. M. Davidson and C. Triggs, *J. Chem. Soc., A*, 1324 (1968).

TABLE III  
OXIDATION OF SUBSTITUTED AROMATICS WITH  
VANADIUM OXYTRICHLORIDE

Substrate	Product	Yield %
Phenol	Diphenol	
1-Naphthol	4,4'-Dihydroxybinaphthyl	56
2-Naphthol	2,2'-Dihydroxybinaphthyl	65
<i>m</i> -Cresol	Unidentified polycresol	
2,6-Xylenol	3,3',5,5'-Tetramethyl-4,4'-diphenoquinone	38
Diphenylamine	Unidentified polymer	
Ethyl benzoate <sup>a</sup>	No reaction	

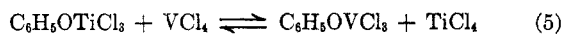
<sup>a</sup> At 65°.

with polymeric products. The use of water as solvent offers certain advantages; for example, the vanadium oxytrichloride can be used in catalytic amounts and reoxidized with potassium chlorate.

### Discussion

Although the mechanism for the coupling of phenols with vanadium tetrachloride or vanadium oxytrichloride has not been completely elucidated, certain factors are evident. The reactivity of free phenols and the relative inertness of *ortho*-substituted phenols and aromatic hydrocarbons indicates that the hydroxy group on phenol has a significant influence on the course of the reaction. This can be attributed to both the higher reduction potential of the free phenols and the necessity for formation of oxygen to vanadium bonds. A considerable amount of evidence has been obtained which indicates that vanadium phenoxides with complex structures are formed during the reaction. The fact that more hydrogen chloride is evolved than can be accounted for solely by the loss of two molecules of hydrogen chloride per molecule of dimer produce strongly suggests that vanadium phenoxides are present. The deuterium oxide quenching experiments in which no carbon-deuterium bonds were detectable is also suggestive. Further support for the intermediacy of vanadium-oxygen bonds was obtained in an experiment in which trichlorotitanium phenoxide was allowed to react with vanadium tetrachloride to afford a 41% yield of 4,4'-diphenol (eq 4) and a 38% yield of hydro-

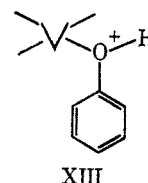
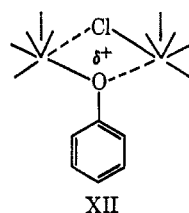
gen chloride. The lack of influence by the trichlorotitanium substituent points to the following exchange reaction 5 in which the trichlorovanadium phenoxide is



then the active coupling species or an intermediate leading to one. If the normal reaction pathway involved a Friedel-Crafts-type metalation of the aromatic nucleus, then one would expect the trichlorotitanium substituent to have a significant effect on the course of the reaction.

The oxidative coupling is believed to occur by a rearrangement of electrons in a complex containing at least two phenoxide (or phenol) residues and at least one metal center. The selectivity of the coupling reaction may be interpreted in terms of a polar or ionic transition state in which charges are developed in the aromatic rings. Intermediates related to XII and XIII could

serve to polarize the aromatic ring and distribute a quasicationic charge to the 2 and 4 positions of one of the aromatic residues. The existence of intermediates such as XIII is suggested by the data on the evolution



of hydrogen chloride from the reaction mixture (Table II). It is also plausible that vanadium to carbon bonds of either the  $\pi$  or  $\sigma$  types are involved in the coupling process. Organovanadium compounds of the types  $\text{C}_6\text{H}_5\text{VOCl}_2$  and  $\text{C}_6\text{H}_5\text{VCl}_3$  were previously prepared in these laboratories and were found to decompose spontaneously to biphenyl and the lower valence vanadium halide<sup>7</sup> (eq 6).



Mention should be made at this point of some interesting results obtained by other workers with molybdenum oxytetrachloride. Larson and Moore have found that molybdenum oxytetrachloride oxidizes aromatic compounds with specific coupling at the *para* positions.<sup>8</sup> For example, reaction of molybdenum oxytetrachloride with refluxing phenol afforded a 19.6% yield of 4,4'-diphenol and reaction with refluxing benzene gave a 40% yield of poly-*p*-phenylene. Under our conditions (admixture of equimolar quantities of phenol and molybdenum oxytetrachloride in carbon tetrachloride), the following product distribution, accounting for 65% of the initially charged phenol, was obtained after hydrolysis: 54% phenol, 12% *o*- and *p*-chlorophenols, 5% *o,o'*-diphenol, 1% *p,p'*-diphenol, and 28% *p,p'*-diphenol. The remaining 35% was made up of polymeric products.

At present, the outstanding mechanistic questions seem to be the following: (1) whether the reactive intermediates leading to coupled products are vanadium phenoxides or vanadium to carbon bonded species; (2) whether oxidation occurs by a two-electron or a one-electron transfer from phenol to a metal center; and (3) what factors are responsible for the incomplete oxidation of phenol to diphenol. One can regard the resolution of these mechanistic problems as a useful, although difficultly attainable, goal. Clearly, vanadium tetrachloride and vanadium oxytetrachloride are extremely useful reagents for the preparation of diphenols and diaminobiphenyls by direct coupling.

### Experimental Section

**General Reaction Procedure.**—Into a 250-ml, two-neck, round flask equipped with a magnetic stirrer was placed 100 ml of dry solvent, usually carbon tetrachloride. One neck was connected to a bubble counter filled with carbon tetrachloride, and the other was plugged with a serum stopper. After 40 mmol of aromatic substrate was introduced, the system was thoroughly purged with nitrogen and 40 mmol of transition

(7) W. L. Carrick, W. T. Reichle, F. Pennella, and J. J. Smith, *J. Amer. Chem. Soc.*, **82**, 3887 (1960).

(8) M. L. Larson and F. W. Moore, *Inorg. Chem.*, **5**, 801 (1966).

metal compound solution was then introduced *via* a hypodermic syringe. After the initial reaction was complete, the mixture was stirred for an additional hour and then decomposed with 100 ml of sulfuric acid. If an insoluble reaction product was formed, it was filtered, crystallized from a suitable solvent, and identified by its melting point and ir spectrum. The carbon tetrachloride layer was separated and evaporated to dryness. The dry residue was treated with an excess of hot water to wash away any starting material. The product was purified by crystallization or sublimation and identified by its melting point and ir spectrum.

**Reaction of Phenol with Vanadium Tetrachloride.**—Into the apparatus described above was placed 3.8 g (40 mmol) of distilled phenol and 100 ml of dry carbon tetrachloride. After the system was purged with nitrogen, the stirring was started and 40 mmol of vanadium tetrachloride in 15 ml of carbon tetrachloride was introduced. The reaction mixture turned dark, vigorous evolution of hydrogen chloride started, and an insoluble dark residue formed.<sup>9</sup> An exotherm of about 10° accompanied the reaction. The evolution of hydrogen chloride stopped after about 5 min. After the reaction mixture was stirred for a total of 1 hr, it was decomposed with 100 ml of sulfuric acid; a greenish blue acidic layer, colorless carbon tetrachloride layer, and a white crystalline interlayer developed. The white solid was filtered, washed with water, and recrystallized from alcohol to yield 1.1 g (30%) of 4,4'-dihydroxybiphenyl, mp 275–278° (lit.<sup>10</sup> mp 274–275°). The ir spectrum and vpc retention times were identical with those for an authentic sample of 4,4'-dihydroxybiphenyl.

In a second experiment, the reaction mixture was worked up by pouring it into 50 ml of 1 *N* hydrochloric acid and extracting exhaustively with ether. Vpc analysis using a 3-m column packed with 3% O.V. 1 on Chromosorb P indicated that the following components were present: 39% phenol, 4% 2,2'-dihydroxybiphenyl, 18% 2,4'-dihydroxybiphenyl, 34% 4,4'-dihydroxybiphenyl, and 5% higher boiling products.

**Reaction of *N,N*-Dimethylaniline with Vanadium Tetrachloride.**—Into the apparatus described under the general reaction procedure was placed 100 ml of dry carbon tetrachloride and 5.1 ml (40 mmol) of distilled *N,N*-dimethylaniline. After the system was purged with nitrogen the stirring was started and 40 mmol of vanadium tetrachloride was added. A dark precipitate formed immediately. The reaction mixture was stirred for 1 hr and then decomposed with 100 ml of sulfuric acid. The aqueous layer was separated and basified with 10% sodium hy-

droxide. The dark green residue was filtered, washed with water, and dried. This residue was then extracted with ether in a soxhlet for 2 days. On evaporation of ether, 2.2 g of *N,N,N',N'*-tetramethylbenzidine was obtained: mp 194° (crystallized from alcohol).

**Reaction of 1-Naphthol with Vanadium Oxytrichloride.**—Into the apparatus described under the general reaction procedure was placed 2 g (13 mmol) of 1-naphthol and 50 ml of dry benzene. The system was purged with nitrogen and 1 ml (10.5 mmol) of vanadium oxytrichloride was added. Vigorous evolution of hydrogen chloride and formation of dark residue followed. After the mixture was stirred for 15 min, 50 ml of sulfuric acid was added. The acidic layer turned blue, and a white crystalline residue settled out. This residue was filtered and dried to yield 0.92 g (56%) of 4,4'-dihydroxybinaphthyl, mp 297–229° (lit.<sup>10</sup> mp 300°).

**Reaction of 1-Naphthol with Vanadium Tetrachloride.**—Into the apparatus described in the general reaction procedure was placed 5.6 g (40 mmol) of 1-naphthol and 100 ml of dry benzene. After the apparatus was purged with nitrogen, the stirring was started and 40 mmol of vanadium tetrachloride in 14 ml of carbon tetrachloride was added. Vigorous evolution of hydrogen chloride was accompanied by the formation of dark precipitate. After 1 hr of stirring, the reaction mixture was decomposed with 50 ml of 1 *N* sulfuric acid. The residue was filtered, washed with water, and crystallized from alcohol to yield 2.3 g (40%) of 4,4'-binaphthol, mp 295–298° (lit.<sup>10</sup> mp 300°).

**Determination of Hydrogen Chloride Yield in the Reaction of Phenol with Vanadium Tetrachloride.**—Phenol (40 mmol) and vanadium tetrachloride (40 mmol) were allowed to react following the general procedure. A trap containing 200 ml of distilled water was connected to the flask to capture the hydrogen chloride evolved during the reaction. After the reaction was complete, nitrogen was bubbled through the reaction mixture for 1.5 hr to sweep the remaining hydrogen chloride into the water trap. The contents of the trap were titrated with 44.5 ml of 1.051 *N* sodium hydroxide to the phenolphthalein end point. The reaction yielded 46.77 mequiv of hydrogen chloride (HCl/VCl<sub>4</sub>, 1.2, and HCl/phenol, 1.2).

The reaction mixture was hydrolyzed with 50 ml of 1 *N* sulfuric acid and *p,p'*-diphenol was separated. The yield of *p,p'*-diphenol after washing with carbon tetrachloride was 1.4 g (38%).

The same procedure was used for the remaining experiments in Table II.

**Registry No.**—Vanadium tetrachloride, 7632-51-1; vanadium oxytrichloride, 7727-18-6; *N,N,N',N'*-tetramethylbenzidine, 366-29-0.

(9) In one experiment, this residue was removed by vacuum filtration under nitrogen. *Anal.* Calcd: C, 31.33; H, 2.40; Cl, 20.83; O, 7.37.

(10) Handbook of Chemistry and Physics, C. D. Hodgman, R. C. Weast and S. M. Selby, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1959.