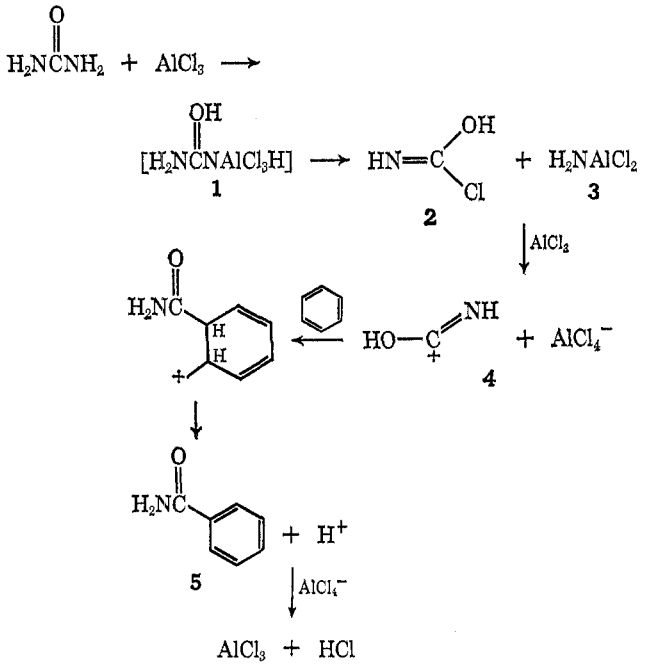
SCHEME I



Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer. Melting points were uncorrected and obtained by using a Hoover capillary melting point apparatus.

Synthesis of Arylamides.—The general method for the preparation of these compounds was as follows. Urea, 24 g (0.40 mol), was carefully added to 113 g (0.85 mol) of anhydrous aluminum chloride. Care must be exercised during this addition because an exothermic reaction results. The temperature of the reaction was controlled by the rate of urea addition. However, the reaction temperature was usually kept in the range of 90–100°. After the addition of the urea was complete, the resulting mixture was cooled to 25° and 0.35 mol of the appropriate aromatic compound was added. The reactants were stirred for 2–18 hr at 50–70°, cooled, and slowly poured into 500 ml of ice water. Because substantial amounts of unchanged aluminum chloride are present in the reaction mixture, extreme care must be exercised while decomposing it in the ice water. Pentane (500 ml) was added, and the two phases filtered. Arylamides which are water- and pentane-insoluble remain as a solid on the filter paper. Water-soluble arylamides (*e.g.*, 4-methylbenzamide) were ether extracted from the water phase. The ether extracts were dried over anhydrous calcium sulfate, the ether was evaporated, and the residues were recrystallized from benzene or water to give pure arylamides.

Properties of Arylamides.—The arylamides were characterized by their elemental analyses, infrared spectra, and comparisons of their respective melting points with literature values.

Table I summarizes the results of the elemental analyses and the comparative melting point data. The infrared spectra of the arylamides exhibited the following characteristic absorption bands: ir (Nujol) 3450–3320 cm^{-1} (free NH), 3210–3160 cm^{-1} (associated NH), 1660–1640 cm^{-1} (amide I band), 1620–1610 cm^{-1} (amide II band), and 1560 cm^{-1} (phenyl nucleus).

Hydrolysis of 3,4-Dimethylbenzamide.—A mixture of 200 mg (1.30 mmol) of 3,4-dimethylbenzamide, mp 105–106° (Table I), and 10 ml of 3 *N* NaOH was heated at reflux for 6 hr, cooled, and acidified with 4 ml of concentrated HCl to give 192 mg of crude acid, mp 152–156°. Sublimation of this material at 60° *in vacuo* afforded 163 mg (82%) of 3,4-dimethylbenzoic acid, mp 162–163°; ir spectrum was identical with that of 3,4-dimethylbenzoic acid.[8]

(8) "Sadtler Standard Spectra," No. 24490, Microfilm Edition, Sadtler Research Laboratories, Inc., 1969.

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.48; H, 6.67.

Registry No.—Aluminum chloride, 7446-70-0; 3-chloro-4-methylbenzamide, 24377-95-5.

The Oxidation of 2,6-Disubstituted Phenols with Isoamyl Nitrite. A Simple Preparation of Diphenoquinones

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Phenol oxidation by alkyl nitrites has not been extensively studied. The reported oxidations have been concerned chiefly with 2,4,6-trisubstituted compounds.[2] In Bacon's survey of oxidants for 2,6-dimethylphenol, the reaction of isoamyl nitrite (60 mol) with phenol (1 mol) in water gave 2,2′,6,6′-tetramethyl-4,4′-biphenol (20%) and 3,3′,5,5′-tetramethyldiphenoquinone (37%).[3] When the mole ratio was reduced to 7.5:1 in ethyl alcohol, the diphenoquinone (6%) was obtained along with the major product, *p*-nitroso-2,6-dimethylphenol (75%).

We have extended this oxidation to a convenient synthesis of certain diphenoquinones by oxidation of 2,6-disubstituted phenols with isoamyl nitrite in methylene chloride. The reaction is run for 18–24 hr at ambient temperature and the insoluble product is isolated by filtration. Table I gives the results for a number of phenols; yields are in the 50–65% range. When sterically hindering groups such as *t*-butyl or deactivating groups such as chlorine occupy the *ortho* positions, the yields are lower. The higher oxidation potential of 2,6-dichlorophenol completely inhibited its oxidation to the diphenoquinone whereas 2-chloro-6-phenylphenol gave a small yield of quinone. The yields were improved by using chloroform at reflux for 2.5 hr.

TABLE I

2,6-Disubstituted phenol	Diphenoquinone: % yield of CH_2Cl_2	Diphenoquinone: Mp, °C	Mol of oxidant/mol of phenol
Dimethyl-	53[a]	205.5–208[b]	2.1
Diphenyl-	58	283–285[b]	3.0
Methyl phenyl-	51	202–204[b]	2.5
Dimethoxy-	65	288–290[b]	2.5
Di-*t*-butyl-	16	242.5–244[b]	3.3
Chloro phenyl-	10[c]	287.5–288.5	3.0
Dichloro-			

[a] 64% yield obtained in $CHCl_3$. [b] The infrared spectrum was identical with that of the authentic material. [c] 21% yield obtained in $CHCl_3$.

(1) Food and Drug Administration, Bureau of Drugs, Washington, D. C. 20204.

(2) (a) J. Thiele and H. Sichwerde, *Ann.*, **311**, 363 (1900). (b) V. V. Ershov and G. A. Zlobina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2138 (1964).

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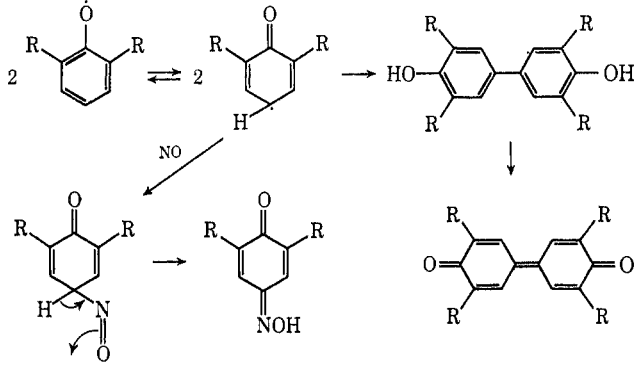
The reduction in yield when a *t*-butyl group is present is probably due to two factors: the increased solubility of diphenoquinones containing such groups and competing oximination. The isolation of 2,6-di-*t*-butyl-4-oximinobenzoquinone, which has been reported both as *p*-nitroso-2,6-di-*t*-butylphenol[4] or as the oxime,[5] and recently has been shown to exist as the oxime,[6] from the oxidation of 2,6-di-*t*-butyl phenol supports the second factor.

The reaction path very likely involves the production of phenoxy radicals. Ershov and Zlobina were able to record the esr signal for 2,4,6-trisubstituted phenoxy radicals when the corresponding phenols were oxidized with alkyl nitrites.[2b] They proposed that an alkoxy radical, produced by scission of the alkyl nitrite, abstracted hydrogen from the phenol to give the phenoxy radical. Some support for the intermediacy of an alkoxy radical is contained in the thermal decomposition of 2-octyl nitrite at 100°.[7] The products are the 2-octyloxy and the nitric oxide radicals. In the case of the 2,6-disubstituted phenols in Table I, the free *para* positions would allow dimerization to the biphenol.[8] Subsequent oxidation of the biphenol would give the diphenoquinone, Scheme I. The total process involves the removal of two hydrogen atoms from each mole of phenol to give the diphenoquinone, necessitating at least 2 mol of oxidant/mol of phenol. The formation of oxime in the case of 2,6-di-*t*-butylphenol can be explained by the combination of nitric oxide and phenoxy radicals (Scheme I).

SCHEME I



Experimental Section[9]

3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone.—An example of the general method is given for 2,6-dimethylphenol. 2,6-Dimethylphenol (1.83 g, 0.015 mol) was dissolved in 50 ml of methylene chloride and isoamyl nitrite added (4.3 ml, 0.032 mol). After stirring at ambient temperature for 24 hr, the reaction was worked up by cooling and filtering. The red crystals obtained were washed with several portions of cold methylene chloride and dried to give 0.976 g of product (53%), mp 205.5–208° (lit.[10] mp 207–210°). The ir spectrum was essentially identical with that of the authentic material.

3,3′,5,5′-Tetra-*t*-butyl-4,4′-diphenoquinone.—2,6-Di-*t*-butylphenol (3.09 g, 0.015 mol) and isoamyl nitrite (6.72 ml, 0.050 mol) were dissolved in 20 ml of methylene chloride. The solution was stirred at ambient temperature for 28 hr and then heated at reflux for 15 hr. The solvent was distilled to leave a semisolid mass. This was treated with acetic acid and filtered. The filter cake was washed with acetic acid and dried to give 0.503 g of title compound (16.3%), mp 242.5–244° (lit.[11] mp 245–247°). The ir spectrum was essentially identical with that of the authentic material.

2,6-Di-*t*-butyl-4-oximino-*p*-benzoquinone.—2,6-Di-*t*-butylphenol (3.09 g, 0.015 mol) was dissolved in 25 ml of methylene chloride and isoamyl nitrite (5.10 ml, 0.0375 mol) was added. The reaction solution was stirred at ambient temperature for 27 hr and then the solvent was removed under vacuum (20 mm). The gummy dark residue was treated with 20 ml of methyl alcohol and filtered to remove some brown solid. The filtrate was warmed under vacuum to remove the solvent and the dark oil which remained was extracted with hot hexane. The hexane was concentrated and cooled to give 0.273 g of yellow crystals, mp 205–207°. Further hexane extraction of the dark gum gave an additional 0.370 g of yellow crystals, mp 199–205°. The two batches were combined and recrystallized from hexane to give 0.630 g (18%) of title compound, mp 213–214° (lit.[5] mp 219–220°). The ir spectrum contained a broad band at 3320 cm^{-1} (–OH) and a sharp band at 1600 cm^{-1} (C=N).

3,3′-Dichloro-5,5′-diphenyl-4,4′-diphenoquinone.—2-Chloro-6-phenylphenol (2.04 g, 0.01 mol) was dissolved in 22 ml of methylene chloride and isoamyl nitrite was added (4.0 ml, 0.03 mol). The solution was stirred at ambient temperature for 24 hr at which time some red solid was present. The mixture was heated at reflux for 2 hr, cooled, and filtered. The filter cake was washed with cold methylene chloride and dried under vacuum to give purple-red crystals, 0.21 g (10%), mp 282–283°. This was recrystallized from chloroform to give mp 287.5–288.5°; ir (KBr) 1610 cm^{-1} (C=O). *Anal.* Calcd for $C_{24}H_{14}Cl_2O_2$: C, 71.13; H, 3.48; Cl, 17.50. Found: C, 70.5; H, 3.77; Cl, 17.7.

Registry No.—Isoamyl nitrite, 110-46-3; 2,6-dimethylphenol, 576-26-1; 2,6-diphenylphenol, 2432-11-3; 2-methyl-6-phenylphenol, 17755-10-1; 2,6-dimethoxyphenol, 91-10-1; 2,6-di-*t*-butylphenol, 128-39-2; 2-chloro-6-phenylphenol, 85-97-2; 2,6-dichlorophenol, 87-65-0; 3,3′-dichloro-5,5′-diphenyl-4,4′-diphenoquinone, 24378-09-4.

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(6) R. K. Norris and S. Sternhell, *Aust. J. Chem.*, **22**, 935 (1969).
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(9) Melting points are uncorrected. The authentic diphenoquinones were provided by Drs. A. S. Hay and D. M. White of this laboratory. All ir spectra were obtained on a Perkin-Elmer Model 337 instrument.
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β-Keto Sulfoxides. IX. Conversion into Acetylenic Sulfoxides and Sulfones[1]

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We have previously described the conversion of esters to β-keto sulfoxides (reaction 1)[2] and the reduction of the β-keto sulfoxide to the hydroxy sulfide (reaction 2),[3] which may be dehydrated to give the vinyl sulfide (reaction 3).[3] Attempts to convert β-(methylmercapto)styrene to the acetylenic sulfide by the standard bromination–dehydrobromination technique[4]

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