DCNQ, cyclization does not occur unless another mechanism is offered (*e.g.*, Ullman reaction).

While this investigation had dealt solely with the base-catalyzed condensation of 2-naphthol with DCNQ, these mechanistic aspects may be generally applicable to other hydroxy aromatic systems.

Experimental Section[5]

Preparation of 1-[2-(3-Chloro-1,4-naphthoquinone)]-2-naphthol (3).—A suspension of 2-naphthol (1.44 g, 0.01 mol), DCNQ (2.27 g, 0.01 mol), and sodium acetate (0.82 g, 0.01 mol) in 2-propanol (50 ml) was heated at reflux for 10 hr. The originally yellow solution turned red shortly after heating commenced. The red solution was allowed to cool to room temperature and a red, crystalline solid was collected by suction filtration. Recrystallization from 2-propanol provided 1.2 g (36%) of **3** as red needles, mp 178–179°, ir (dioxane) 3575 (OH), 1675 cm^{-1} (C=O).

Anal. Calcd for $C_{20}H_{11}O_3Cl$: C, 71.76; H, 3.31; Cl, 10.59. Found: C, 71.45; H, 3.20; Cl, 10.51.

Preparation of Dinaphtho[2,1:2′,3′]furan-8,13-dione (2) from Compound 3.—Compound **3** (0.490 g, 1.49 mmol) was refluxed for 2 hr in pyridine (25 ml) and the solution was allowed to cool to room temperature. The yellow-orange crystalline compound, which crystallized from the pyridine solution, was then collected by suction filtration. Compound **2**, 0.31 g (67%, mp 272–273° (lit.[2] mp 271–272°), was obtained after recrystallization from 2-propanol.

Registry No.—**3**, 33835-18-6; 2,3-dichloro-1,4-naphthoquinone, 117-80-6.

Acknowledgment.—Technical assistance by Richard L. Schank and discussions with W. H. H. Gunther, B. Grushkin, R. J. Gruber, and H. A. Six are gratefully acknowledged.

(5) Melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer 247 grating spectrophotometer.

Reaction between Arylnitrones and Arylnitroso Compounds

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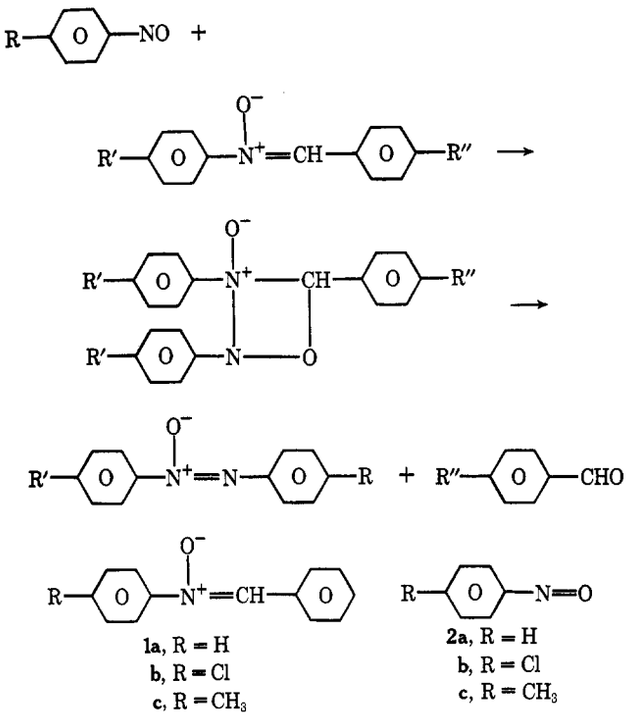
For another study we required a number of *p,p′*-disubstituted azoxybenzenes. The few reported methods for the synthesis of pure isomers[1a,b] were not entirely suitable for the preparation of the desired compounds, and we were interested in finding a more general procedure.

Alessandri[2] reported the formation of azoxybenzene in the reaction between nitrosobenzene and a nitrone. In a recent publication, Taylor and Buntrock[3] postulated a cyclic intermediate in a similar reaction which

(1) (a) T. E. Stevens, *J. Org. Chem.* **29**, 311 (1964). (b) L. C. Behr, E. G. Alley, and O. Livand, *ibid.*, **27**, 65 (1962).
(2) L. Alessandri, *Gazz. Chim. Ital.*, **54**, 426 (1924).
(3) E. C. Taylor and R. E. Buntrock, *J. Org. Chem.*, **36**, 634 (1971).

SCHEME I



suggested the reaction mechanism shown in Scheme I. This reaction appeared to be a potentially attractive route to unsymmetrically substituted azoxybenzenes.

In our investigation of the reaction between nitrosobenzene and *N*,α-diphenylnitrone, we found that the reaction went to completion in untreated chloroform after several hours at ambient temperature, but that no reaction occurred in dimethylformamide, dimethyl sulfoxide, acetonitrile, or benzene under the same conditions.[4] We also found that the reaction was catalyzed by trifluoroacetic acid in all solvents and that the reaction was inhibited in dry, acid-free chloroform.

The reactions between nitrones (**1**) and nitrosobenzenes (**2**) were conducted in untreated chloroform, presumably containing a catalytic amount of acid. Column chromatography (alumina) of the products of the reaction of **1b** and **2a** gave three fractions, which were identified by comparison with authentic samples as azoxybenzene, 4,4′-dichloroazoxybenzene, and a mixture of 4- and 4′-chloroazoxybenzene in the ratio of 0.9:0.9:1. The reactions between **1a** and **2b** yielded the same product ratio, indicating that both reactions proceeded through the same intermediates.

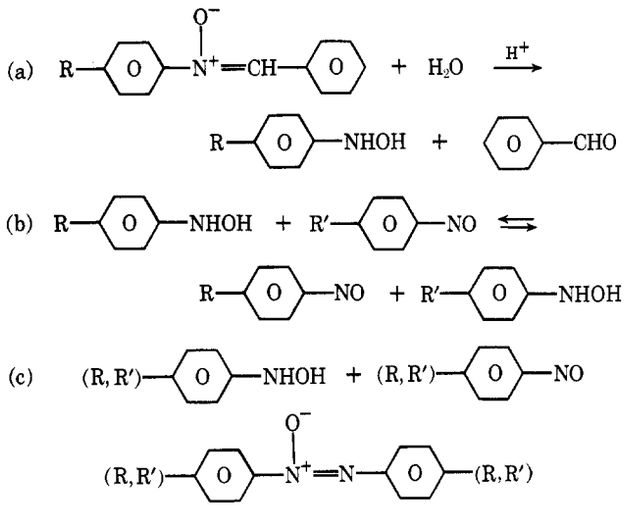
Similar results were obtained for the reactions of **1c** and **2a** and **1a** with **2c**. The three isolated fractions were azoxybenzene, 4,4′-dimethylazoxybenzene, and a mixture of 4- and 4′-methylazoxybenzene in the ratio of 0.95:0.96:1.

Reactions between *p*-chlorophenylhydroxylamine and **2a** in chloroform gave the same distribution of azoxy products as in the reaction between **1b** and **2a**. Similar results were obtained in the reaction between *p*-methylphenylhydroxylamine and **2a** in chloroform.

These results rule out the cyclic mechanism shown in Scheme I. A more plausible mechanism involves the acid-catalyzed hydrolysis of nitrone to give the phenyl-

(4) Previous authors conducted their reactions in chloroform. See ref 2 and 3.

SCHEME II



hydroxylamine which then equilibrates with the phenylnitrosobenzene. The phenylhydroxylamines and phenylnitroso compounds then react irreversibly to give azoxy products (Scheme II). The kinetics and mechanism of the latter reactions have previously been investigated.[5a,b]

In order to examine the possibility that α-anilino-*N*-phenylnitrones[3] might react differently than **1**, α-*p*-toluidino-*N*-tolylnitrone (**3**) was treated with nitrosobenzene in chloroform in the dark for 5 days at ambient temperature. In addition to *p*-methylformanilide, azoxybenzene, 4,4′-dimethylazoxybenzene, and a mixture of 4- and 4′-methylazoxybenzene were formed. This suggests that the α-anilino-*N*-phenylnitrones react *via* a mechanism similar to α-phenyl-*N*-phenylnitrones (Scheme II).

Experimental Section

The aryl hydroxylamines were prepared by the procedure of Kamm.[6] Nitrosobenzene was purchased from the Aldrich Chemical Co. The other nitrosobenzenes were prepared using the procedure of Barrow.[7] α-*p*-Chlorophenyl-*N*-phenylnitrone and α-*p*-tolyl-*N*-phenylnitrone were synthesized using the reported methods.[8a,b]

α-*p*-Toluidino-*N*-*p*-tolylnitrone.—Using the procedure of Taylor,[3] a solution of *p*-methylnitrosobenzene (2.4 g, 0.92 mol) and *p*-methylmethylene aniline (3.6 g, 0.03 mol) in 70 ml of chloroform was stoppered and kept in the dark for 70 hr. The chloroform was removed under reduced pressure. The solid remaining was taken up and recrystallized from benzene, yield 1.9 g (35%), mp 129–130°.

Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.96; H, 6.71; N, 11.66. Found: C, 74.77; H, 6.79; N, 11.42.

The reaction below illustrates the general procedure used in the reactions of arylnitrones with the nitrosobenzenes.

Reaction of α-Phenyl-*N*-*p*-chlorophenylnitrone with Nitrosobenzene.—A solution of α-phenyl-*N*-*p*-chlorophenylnitrone (3.45 g, 0.015 mol) and nitrosobenzene (1.5 g, 0.015 mol) in 75 ml of chloroform was stoppered and placed in the dark for 70 hr. At the end of that time no nitrone remained as evidenced by glpc. Three products were formed. The products were separated by preparative glpc and found to be azoxybenzene, 4- and 4′-chloroazoxybenzene, and 4,4′-dichloroazoxybenzene by superimposing their ir spectra with the ir spectra of known samples. The three products were formed in the ratio of 0.9:1:0.9. Benzaldehyde was the only other product formed.

Reaction of α-*p*-Toluidino-*N*-*p*-tolylnitrone with Nitrosobenzene.—Using the procedure of Taylor and Buntrock,[3] a mixture of α-*p*-toluidino-*N*-*p*-tolylnitrone (0.48 g, 0.0002 mol) and nitrosobenzene (0.22 g, 0.002 mol) in 30 ml of chloroform was allowed to stand in the dark for 5 days. Analysis by glpc showed that the nitrone was 75% reacted. The four products found were *p*-methylformanilide, azoxybenzene, 4- and 4′-methylazoxybenzene, and 4,4′-dimethylazoxybenzene, formed in the ratio of 7:3:1.8:1.

Registry No.—α-*p*-Toluidino-*N*-*p*-tolylnitrone, 33905-35-0; α-phenyl-*N*-*p*-chlorophenylnitrone, 5909-74-0; nitrosobenzene, 586-96-9.

(5) (a) Y. Ogata, M. Tsuchida, and Y. Takgi, *J. Amer. Chem. Soc.*, **79**, 3397 (1957). (b) G. A. Russell and E. J. Geels, *ibid.*, **87**, 122 (1965).

(6) O. Kamm, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., p 445.

(7) F. Barrow and F. J. Thorneycroft, *J. Chem. Soc.*, 773 (1939).

(8) (a) R. E. Erickson and T. M. Myszkewicz, *J. Org. Chem.*, **30**, 4236 (1965). (b) S. L. Larsen, G. Schroll, S. O. Lawesson, J. H. Bowie, and R. G. Cooks, *Tetrahedron*, **24**, 5193 (1968).

On the Friedel–Crafts Benzoylation and Acylation of Kojic Acid

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Despite reports to the contrary, we believe that Friedel–Crafts acylation or aroylation reactions of kojic acid (**1**, 2-hydroxymethyl-5-hydroxy-4*H*-pyran-4-one)[1] under Friedel–Crafts conditions are yet to be accomplished.

Woods reported that treatment of **1** with benzoyl chloride and aluminum chloride in carbon disulfide yielded 6-benzoylkojic acid (**2**), mp 188°.[2] Following the published procedure, we obtained a crystalline monobenzoylated product, mp 180–181°, mol wt 264 (mass spectrum), which gave a positive $FeCl_3$ test. That it was not the anticipated Friedel–Crafts product but rather the benzoate ester **3** (lit.[3] mp 180–181°) was demonstrated by comparing the nmr spectra of **1** and **3**, which showed the deshielding of the methylene protons from 4.50 to 5.20 ppm by the benzoate group, and which confirmed the presence of two pyrone ring protons (Table I). Although the signals for the phenyl protons overlapped that of the C-6 proton, the latter was clearly visible in the integration.

Woods' structural assignment for his benzoylated product rested largely on the results of a Clemmensen reduction, which yielded a product different from the starting material, and the reaction was therefore taken to represent the reduction of the benzoyl ketone. While it is entirely possible that Woods had actually obtained **2**, and that its synthesis was very sensitive to minor changes in reaction conditions, we also considered the possibility that he was dealing with **3** and that its reduction had taken an unforeseen course. Treatment of **3** in the conditions of the Clemmensen reduction[1] yielded some benzoic acid, probably resulting from hydrogenolysis.[3] A neutral fraction which we could not crystallize was also obtained. It was acetylated to yield a product, mp 91–92°. Its molecular weight of 168 (mass spectrum) and nmr ($CDCl_3$), which consisted

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(2) L. L. Woods, *J. Amer. Chem. Soc.*, **74**, 1105 (1952).

(3) A. Beelik and C. B. Purves, *Can. J. Chem.*, **33**, 1361 (1955).