at 125°) of the less polar fraction obtained in the preceding reaction showed three components with retention times of 2.3 min (45%, component A), 5.7 min (50%, component B), and 9.2 min (5%, component C). These materials were separated by preparative gc (Carbowax 20M + KOH column at 180°) and were assigned structures **3**, **4**, and **5** on the basis of spectral data (obtained for gas chromatographically homogeneous samples): component A, 1-hydroxymethyl-5-methyl-5-vinylcyclopentene (**3**); component B, 2,6-dimethyl-*trans*,*trans*-2,6-nonadien-1-ol (**4**); and component C, 6-methyl-*trans*-6-nonen-2-yn-1-ol (**5**).

The alcohol **3** showed the following nmr spectrum (CCl_4): 1.15 (singlet, 3 H, CH_3–), 1.55–1.95 (multiplet, 2 H, $-CH_2-$, C-4), 2.1–2.45 (multiplet, 2 H, $-CH_2-$, C-3), 3.78 (singlet, 1 H, –OH), 3.94 (broad singlet, 2 H, $-CH_2O-$), 4.90 (doublet, J = 18 Hz, 1 H, –CH=C(H)**H**, cis to cyclopentene ring), 4.90 (doublet, J = 10 Hz, 1 H, –CH=C(H)**H**, *trans* to cyclopentene ring), 5.60 (1 H, =CH–, C-2), and 5.81 (doublet of doublets, J = 10, 18 Hz, 1 H, –C**H**=CH_2). The ir spectrum (CCl_4) exhibited bands at 3.05 (s, O–H stretch), 3.40 and 3.50 (s, C–H stretch), 6.10 (m, C=C stretch), 6.90, 7.10, and 7.30 (m, C–H bend), 9.15 (m), 9.70 (s, C–O stretch), 9.95 and 10.9 (s, C–H out of plane deformation, –CH=CH_2), and 12.65 (m). The mass spectrum (20 eV) showed a molecular ion at m/e 138, with prominent peaks resulting from cleavage of the fragments CH_3 (123), H_2O (120), CH_2OH (107), and H_2O + CH_3 (105), as well as other peaks at m/e 96, 94, 92, and 79.

An exact mass determination (AEI MS-9 mass spectrometer) showed the parent peak at m/e 138.1040 (calcd for $C_9H_{14}O$: 138.1044).

The nmr spectrum (CCl_4) of **4** exhibited signals at 0.94 (triplet, J = 7.5 Hz, 3 H, CH_3CH_2-), 1.60 (singlet, 6 H, $CH_3C=$), 1.75–2.3 (multiplet, 6 H, $-CH_2-$, C-4, 5, 8), 2.49 (singlet, 1 H, –OH), 3.85 (singlet, 2 H, $-CH_2O-$), 5.09 (triplet, J = 6 Hz, 1 H, =CH–, C-7), and 5.31 (triplet, J = 6 Hz, 1 H, =CH–, C-3). The ir spectrum (liquid film) revealed bands at 3.00 (s, O–H stretch), 3.40 and 3.50 (s, C–H stretch), 5.98 (w, C=C stretch), 6.90 and 7.20 (m, C–H bend), 7.65 (w), 8.20 (w), 8.65 (w), 9.30 (m), 9.85 (s, C–O stretch), and 11.60 (m).

The nmr spectrum (CCl_4) of **5** exhibited resonances at 0.94 (triplet, J = 7.5 Hz, 3 H, CH_3CH_2-), 1.60 (singlet, 3 H, $CH_3-C=$), 1.8–2.4 (multiplet, 7 H, $-CH_2-$, C-4, 5, 8, and –OH), 4.11 (singlet, 2 H, $-CH_2O-$), and 5.14 (triplet, J = 6 Hz, 1 H, =CH–). The ir spectrum (liquid film) displayed absorbence maxima at 3.0 (s, O–H stretch), 3.40 and 3.50 (s, C–H stretch), 4.37 and 4.40 (w, C≡C stretch), 6.00 (w, C=C stretch), 6.90 and 7.25 (m, C–H bend), 8.15 (m), 8.80 (s), and 9.80 (s, C–O stretch).

Registry No.—**1**, 33835-56-2; **3**, 33835-15-3; **4**, 33835-57-3; **5**, 33835-58-4; dimethylcopperlithium, 15681-48-8.

Mechanism of the Base-Catalyzed Condensation of Naphthols with 2,3-Dichloro-1,4-naphthoquinone

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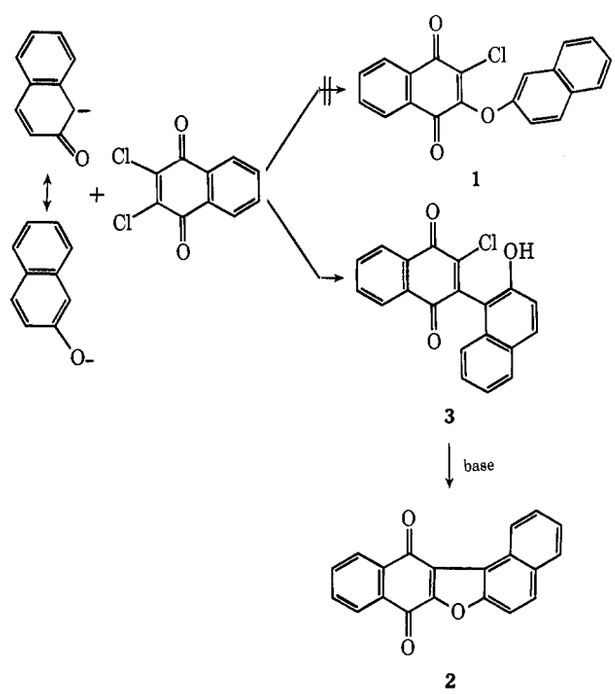
Dinaphthofurandiones, more commonly called benzobrazanquinones, are a series of heterocyclic quinones derived from the base-catalyzed condensation of 1- or 2-naphthol with 2,3-dichloro-1,4-naphthoquinone (DCNQ). The synthesis of dinaphthofurandiones has been reported[1,2] to proceed *via* initial O alkylation of the naphthol anion to yield compound **1**, in the case of 2-naphthol, which then cyclizes, under the reaction conditions, to provide dinaphtho[2,1:2′,3′]furan-8,13-dione (**2**).

Since the reported cyclization of **1** to **2** did not appear reasonable and consistent with the poorly nucleophilic character of the one position of the naphthyl ether, the base-catalyzed condensation of 2-naphthol with DCNQ was investigated.

A red crystalline compound was isolated from the reaction of 2-naphthol with DCNQ in 2-propanol, using 1 mol of sodium acetate, and was proven to be the intermediate by the cyclization to **2** in refluxing pyridine. The intermediate displays an OH stretching frequency at 3575 cm^{-1} in dioxane and treatment of an aqueous acetone solution with alkali produces a blue-colored anion [λ_{max} = 670 mμ ($\epsilon \sim 4000$)], which converts to compound **2** after several minutes at room temperature. Compound **2** decomposes under these basic conditions in a secondary process, providing 2-naphthol and several other compounds which were not identified.

Thus, the intermediate is indicated to be the product of C alkylation (**3**) where a route for ring closure and dinaphthofurandione formation is clearly provided.



Dinaphthofurandione formation then involves initial alkylation on the 2-naphthol anion one position rather than an oxygen, consistent with the greater nucleophilicity of C *vs.* O bases in polar solvents.[3]

This mechanism is also consistent with the inability to form benzo[*b*]naphtho[2,3-*d*]furan-6,11-dione from the condensation of phenol with DCNQ[4] and also the ease of the preparation of certain substituted benzonaphthofurandiones in which meta-substituted phenols are condensed with DCNQ.[2] In these cases strongly electron-donating substituents such as methoxy or dimethylamino, which favor C alkylation, must be employed. If condensation occurs initially by heteroatom attack, as in the case of the addition of aniline to

(1) R. V. Acharya, B. D. Tilak, and M. R. Venkiteswaran, *J. Sci. Ind. Res.*, **16B**, 400 (1957).

(2) M. F. Sartori, *Chem. Rev.*, **63**, 279 (1963).

(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 259.

(4) R. Gruber, private communication.

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.

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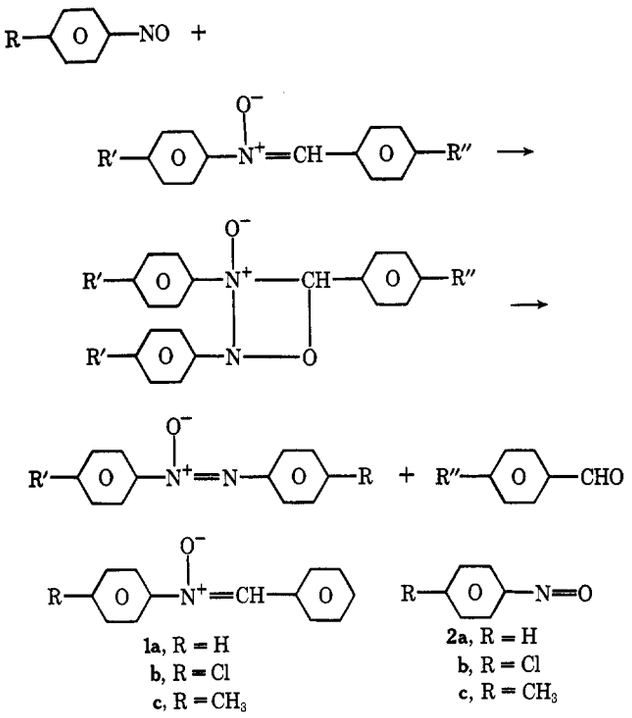
For another study we required a number of *p,p′*-disubstituted azoxybenzenes. The few reported methods for the synthesis of pure isomers[1a,b] were not entirely suitable for the preparation of the desired compounds, and we were interested in finding a more general procedure.

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.