The compound was not acidic. It reacted with benzoyl chloride in benzene after a reflux period of 2 hr. The product, upon analysis, did not have the proper composition for the mono- or dibenzoic ester of any hydroxy compound, alcoholic or phenolic. This test indicated the absence of hydroxyl radicals in the peroxide.

2,6-Dimethyl-3-acetyl-4-pyrone (I). Twelve and four-tenths g. of finely powdered 2,6-dimethyl-4-pyrone, 50 g. of powdered anhydrous aluminum chloride, and 100 ml. of carbon disulfide were quickly and thoroughly shaken in a 500 ml. flask to which was attached a reflux condenser fitted with a gas trap. To the above mixture 15 ml. of acetic anhydride was slowly dropped in. After all the anhydride had been added and the reaction had subsided somewhat the flask was shaken and gently heated for 30 min. The heat was then discontinued and the reaction was allowed to complete itself by standing overnight at room temperature. The carbon disulfide was then decanted from the greyish semisolid and discarded. The residue in the flask was treated with 100 g. of shaved ice followed by 20 ml. of concentrated hydrochloric acid.

The acetylated pyrone was obtained by extracting the resulting solution with benzene and evaporating the solvent. The yield was 3.4 g. The tan solid was recrystallized from boiling heptane and then sublimed to give a pale yellow powder, I, m.p. 125.5–127°.

A mixed melting point of I with an authentic sample of 2,6-dimethyl-4-pyrone was 50–55°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.04; H, 6.06. Found: C, 65.34; H, 6.34.

2,4-Dinitrophenylhydrazone of I. One g. each of I and 2,4-dinitrophenylhydrazine were refluxed together in 100 ml. of ethanol for 5 min., filtered into 100 ml. of water containing 20 drops of concentrated hydrochloric acid, and chilled overnight in the refrigerator. The precipitate was recrystallized from absolute ethanol giving 0.8 g. maroon-purple aggregates which sublimed above 180°, softened above 185°, and melted at 189–191°.

Anal. Calcd. for $C_{15}H_{14}N_4O_6$: N, 16.17. Found: N, 16.30.

2,6-Dimethyl-3-acetyl-4-lutidone (II). One g. of I and 20 ml. of ammonium hydroxide were heated in a pressure bottle at 75° for 1 hr. The solution was filtered, evaporated to dryness on a steam bath to a purple solid, and then sublimed to a pale yellow powder which melted at 226–228.5°, rapid heating.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.47. Found: C, 65.18; H, 7.04; N, 8.24 (Dumas).

2,4-Dinitrophenylhydrazone of II. The 2,4-dinitrophenylhydrazone was prepared by refluxing 1 g. each of II and 2,4-dinitrophenylhydrazine in 50 ml. of absolute ethanol for 5 min. The hydrazone was purified by recrystallizing it twice from absolute ethanol to give 0.3 g., m.p. 203°.

Anal. Calcd. for $C_{15}H_{15}N_5O_5$: N, 20.28. Found: N, 20.44.

2,6-Dimethyl-3-(3,5-dinitrobenzoyl)-4-pyrone [III]. A mixture of 12.4 g. of 2,6-dimethyl-4-pyrone, 21.2 g. of 3,5-dinitrobenzoic acid, 30 g. of fused zinc chloride, and 100 ml. of dry xylene was heated under gentle reflux for 48 hr. The mixture was cooled to −5°C., the xylene decanted, and the black residue vigorously shaken with 100 ml. of boiling water. Extraction with benzene of the residue and evaporation left solid black aggregates which weighed 29 g. The analytical sample, light tan needles, was obtained by recrystallization of 1.5 g. of the compound from 100 ml. of heptane. It melted at 113–114°.

Anal. Calcd. for $C_{14}H_{10}N_2O_7$: C, 52.83; H, 3.16; N, 8.80. Found: C, 52.49; H, 3.40; N, 8.54.

The infrared spectrum[4] of the compound, in chloroform solution, gave an absorption band at 1545 cm.$^{-1}$ for the benzenoid nitro groups. The pyrone structure[5,6] was indicated by a band at 1660 cm.$^{-1}$ An absorption peak at 1715 cm.$^{-1}$ indicated the nonpyrone carbonyl.

2,4-Dinitrophenylhydrazone of the lutidone from III. Two g. of III was dissolved in a small amount of ethanol and then an equal volume of concentrated ammonium hydroxide was added. The solution was allowed to stand overnight in a stoppered flask, following which the mixture was evaporated to dryness on a steam bath. One gram of the grey solid was placed in 100 ml. absolute ethanol along with 1 g. of 2,4-dinitrophenylhydrazine. The mixture was refluxed for 5 min., filtered, and then diluted with an equal volume of water. The orange solid was recrystallized from absolute ethanol, m.p. 199–200.5°.

Anal. Calcd. for $C_{20}H_{15}N_7O_9$: N, 19.71. Found: N, 19.50.

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Reactions Between Chloro-*p*-benzoquinones and β-Naphthol

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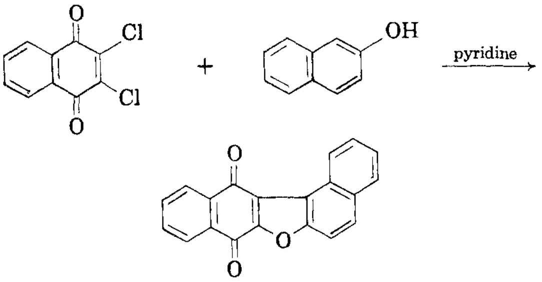
2,3-Dichloro-1,4-naphthoquinone condenses with β-naphthol in the presence of pyridine to give dinaphthylfuranoquinone (I).[1,2]



I

The condensation of chloro substituted *p*-benzoquinones with β-naphthol now has been investigated. Thus, when chloranil was allowed to react with β-naphthol in the presence of pyridine, two molecules of the naphthol condensed with one molecule of the quinone to yield a red crystalline substance believed, by analogy to be naphtho-[*1′,2′-4,5*]furo[*2,3-h*]benz[*c*]dibenzofuran 8,16-quinone (II). This compound was stable toward heat and oxygen and developed a blue color with concentrated sulfuric acid, a color which is characteristic of brazan- and furanquinones.[1,2] Zinc-dust and glacial acetic acid effected its reduction to the corresponding hydroquinone, the isolation of which

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(4) Infrared spectra were determined on a Perkin-Elmer Model 21 Infrared Spectrophotometer.

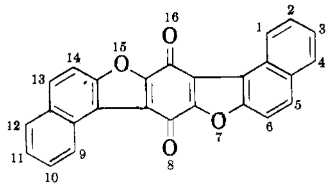
(5) L. L. Woods, *J. Am. Chem. Soc.*, **75**, 3608 (1953).

(6) L. L. Woods, *J. Am. Chem. Soc.*, **77**, 3161 (1955).

(1) B. Eistert, *Ber.*, **80**, 52 (1927).

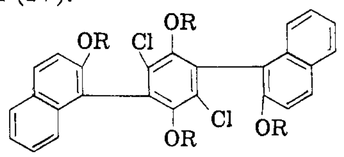
(2) Ng. Ph. Buu Hoï, *J. Chem. Soc.*, 489, 4699 (1952).

has not been attained due to its ready oxidation to the quinone (II) by the action of atmospheric oxygen. Reductive acetylation of II by the action of zinc-dust, acetic acid, and acetic anhydride, yielded the corresponding diacetate. Trials to effect the conversion of II to IV by distillation with zinc-dust or with a zinc-zinc chloride melt[3] were unsuccessful.[4]

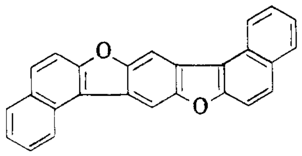


II

Whereas the condensation of chloranil with β-naphthol gave a red crystalline substance, the condensation of 2,5-dichlorobenzoquinone with β-naphthol led to the formation of a colorless substance, believed to have a structure like IIIa. The constitution of IIIa was inferred from the fact that it gave the correct analytical values and the correct molecular weight for the corresponding tetra-acetate (IIIb) obtained by the action of acetic anhydride and fused sodium acetate on IIIa. The ready cyclization of IIIa to the quinone II by boiling in pyridine for a short time involves the elimination of two molecules of hydrogen chloride, followed by oxidation. IIIa, on distillation with zinc-dust in a vacuum, gave a pale yellow substance which analyzed for naphtho[*1′,2′-4,5*]furo[*2,3-h*]benz[*c*]dibenzofuran (IV).



IIIa, R = H
b, R = $COCH_3$



IV

Similarly the condensation of 2-chlorobenzoquinone with β-naphthol in the presence of pyridine yielded a colorless substance; its colorless alcoholic solution turned to deep red by the action of atmospheric oxygen. The condensation product gave a triacetate derivative, showing the presence of three hydroxyl groups. Fractional crystallization of the crude reaction product failed to reveal the presence of any other isomer. The structure of the condensation product is under further investigation.

Though the above mentioned reactions of 2,5-dichloro- and of 2-chlorobenzoquinone with β-naphthol are base catalyzed, yet they can be brought about by the action of dilute sulfuric acid.[5,6]

EXPERIMENTAL

Naphtho(1′,2′-4,5)furo(2,3-h)benz(c)dibenzofuran 8,16-quinone (II). An intimate mixture of chloranil (0.5 g.) and β-naphthol (0.8 g.) was covered with anhydrous pyridine (about 5 ml.) and the hot reaction mixture was refluxed for a few minutes to complete the reaction. The solution was cooled and the dark red needles were collected, washed thoroughly with alcohol, and then recrystallized from pyridine giving shining deep red needles (0.6 g.), m.p. over 350°. The furan-quinone sublimed unchanged at 320°/5 mm. and gave a blue color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{12}O_4$: C, 80.41; H, 3.092. Found: C, 80.68; H, 3.24.

Reductive acetylation of the quinone (II). The quinone (0.2 g.) was heated with a mixture of zinc-dust (1 g.), anhydrous sodium acetate (0.5 g.) and acetic anhydride (30 ml.) for 20 min. Excess glacial acetic acid (about 60 ml.) was added and boiling was continued for a further half hour. The clear filtrate was diluted with water and the precipitated colorless crystals were collected and recrystallized from acetic acid giving slender needles, m.p. 310–12°. Yield, theoretical.

Anal. Calcd. for $C_{30}H_{18}O_6$: C, 75.94; H, 3.82. Found: C, 76.09; H, 4.03.

Zinc-dust distillation of the quinone (II). An intimate mixture of one part of the quinone with ten parts of dry zinc-dust was heated *in vacuo*, and the distillate was collected and purified from pyridine forming red needles which gave a blue color with sulfuric acid identical to that given by the quinone III.

The same experiment was repeated with Clar's zinc-zinc chloride melt[3] and the quinone was recovered unchanged.

Reaction between 2,5-dichloro-p-benzoquinone and β-naphthol. (a) *Pyridine as catalyst.* An intimate mixture of 2,5-dichloro-*p*-benzoquinone (0.5 g.) and β-naphthol (1.0 g.) was treated with few drops of anhydrous pyridine and the hot reaction mixture was cooled and stirred till the dark violet color first formed changed to a dirty white (about 20 min). The resulting sticky product was triturated with a few drops of methanol, filtered quickly and washed several times with benzene. Repeated crystallization from a methanol-benzene mixture furnished colorless short rods or rectangular plates of the hydroquinone (Va) (0.5 g.), m.p. 327° (dec.). A solution of the material in organic solvents changed to deep red when left in the air for a short time.

Anal. Calcd. for $C_{26}H_{16}O_4Cl_2$: C, 67.38; H, 3.45; Cl, 15.33. Found: C, 67.63; H, 3.70; Cl, 15.11.

(b) *Dilute sulfuric acid as catalyst.* A suspension of the dichloroquinone (0.2 g.) and β-naphthol (0.4 g.) in 5% acetic acid (40 ml.) was treated with few drops of 10% sulfuric acid and boiled for 2 min. The dark violet solution was cooled and the precipitate was collected, dried thoroughly, and then crystallized from benzene in colorless rectangular plates (0.3 g.), m.p. and mixed m.p. with the product from (a) 326° (dec.).

Tetraacetate IIIb. Acetylation of (IIIa) by the usual methods furnished a colorless tetraacetate which separated from benzene in colorless prisms, m.p. 285°.

Anal. Calcd. for $C_{34}H_{24}O_8Cl_2$: C, 64.65; H, 3.79; Cl, 11.23; Mol. wt. 631. Found: C, 64.22; H, 4.18; Cl, 11.1; Mol. wt. (Rast), 668.

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(3) E. Clar, *Ber.*, **72**, 1645 (1939).

(4) N. Campell and R. S. Gow, *J. Chem. Soc.*, 1555 (1949).

(5) R. Pummerer, *Ber.*, 60, 1442–51 (1927).

(6) F. M. Dean, A. M. Osman, and A. Robertson, *J. Chem. Soc.*, 11 (1955).

Transformation of IIIa to the quinone (II). A pure sample of the product (IIIa) (0.2 g.) was refluxed in pyridine (7 ml.) for 0.5 hr. The dark red reaction mixture was cooled and the deposited red crystals were collected (0.1 g.) and recrystallized from pyridine into deep red needles, m.p. over 350°. With concentrated sulfuric acid, the mixture gave the blue color characteristic of the quinone (II). The diacetate was prepared by reductive acetylation and proved to be identical with an authentic specimen, m.p. and mixed m.p. 310–312°.

Naphtho(1′,2′-4,5)furo(2,3-h)benz(c)-dibenzofuran (IV). An intimate mixture of the hydroquinone (IIIa) and excess zinc was heated *in vacuo*, and the yellow distillate was further purified by sublimation at 300–320°/2 mm. The product was obtained as pale yellow needles, m.p. 300–302° (dec.), giving an intense blue-violet fluorescence in concentrated sulfuric acid or in the organic solvents.

Anal. Calcd. for $C_{26}H_{14}O_2$: C, 87.15; H, 3.91. Found: C, 86.68; H, 3.87.

Reaction between 2-chloro-p-benzoquinone and β-naphthol. A powdered mixture of the chloroquinone (0.5 g.) and β-naphthol (0.7 g.) was moistened with anhydrous pyridine with stirring and cooling. After a few minutes, the reddish paste was triturated with methanol, filtered, washed several times with light petroleum, and crystallized from benzene in colorless needles (0.3 g.), m.p. 260° (dec.), which acquired a reddish tint when exposed to the air.

Anal. Calcd. for $C_{16}H_{11}O_3Cl$: C, 67.01; H, 3.83; Cl, 12.39. Found: C, 67.31; H, 3.93; Cl, 12.67.

The experiment was repeated using dilute sulfuric acid as a catalyst and the same compound was obtained as shown by m.p. and mixed m.p. determinations.

The reaction product was acetylated in the usual manner and the resulting triacetate was recrystallized from benzene into colorless needles, m.p. 262°.

Anal. Calcd. for $C_{22}H_{17}O_6Cl$: C, 64.0; H, 4.12; Cl, 8.60. Found: C, 63.71; H, 4.18; Cl, 9.10.

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Synthesis of 1-Phenyl-5-aminotetrazole from Benzaldehyde and Hydrazoic Acid

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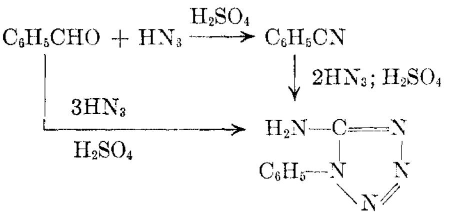
The formation of 1,5-disubstituted tetrazoles by the Schmidt reaction employing excess hydrazoic acid on ketones is well established.[1] Acetone and hydrazoic acid, for example, yield 1,5-dimethyltetrazole[2] although not in the excellent yields originally reported.[3] The action of excess hydrazoic acid on aldehydes has been only slightly studied.[4,5] Benzaldehyde is reported to yield 1-phenyltetrazole[4] while 2-thiophenaldehyde apparently yields 1-(2-thienyl)tetrazole.[5] Since the identification of the products was incomplete in both cases the present investigation was undertaken.

In the presence of concentrated sulfuric acid, equimolar quantities of aldehydes and hydrazoic acid produce nitriles.[1] Under similar conditions 1-substituted-5-aminotetrazoles result from the interaction of nitriles with hydrazoic acid.[6,7] The combination of the two reactions into a single step employing excess hydrazoic acid might be expected to yield 1-substituted-5-aminotetrazoles.

Under similar conditions the reactions of benzaldehyde with one- and three-mole quantities of hydrazoic acid and of benzonitrile with two moles of hydrazoic acid in the presence of concentrated sulfuric acid were studied. From equimolar amounts of benzaldehyde and hydrazoic acid the expected product, benzonitrile, was isolated. Benzonitrile, in turn, reacts with two moles of hydrazoic acid yielding 1-phenyl-5-aminotetrazole. The interaction of benzaldehyde with excess hydrazoic acid also gave 1-phenyl-5-aminotetrazole.



Other aldehydes, including cinnamaldehyde, 1-naphthaldehyde, and *n*-butyraldehyde were examined. However, in no case could an identifiable product be isolated after interaction with excess hydrazoic acid. Intractable tars were the invariable result.

EXPERIMENTAL

Benzonitrile from benzaldehyde. Sulfuric acid (40 g.) was added slowly to a stirred solution of 10.6 g (0.1 mole) of benzaldehyde contained in 110 ml. of 1.0*N* hydrazoic acid in benzene. During the addition the temperature of the mixture was controlled at 35–40°. Evolution of nitrogen ceased in about 30 min. The solution was allowed to stand an additional 30 min. and 200 ml. of ice water was added. After extraction with 2% sodium hydroxide solution the benzene layer was dried over anhydrous sodium sulfate. The benzene was removed by evaporation and the resulting oil was distilled to yield 7.9 g. (77%) of benzonitrile, b.p. 190.5–191°; n_D^{25} 1.5286.

1-Phenyl-5-aminotetrazole from benzonitrile. In a procedure similar to one previously described[7] 40 g. of concentrated

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(1) H. Wolff, "The Schmidt Reaction," Chapter 8 in R. Adams, "Organic Reactions," John Wiley & Sons, New York, 1946, Vol. III, p. 308.

(2) Schmidt, U. S. Patent **1,599,493** [*Chem. Abstr.*, **20**, 3460 (1926)].

(3) Harvill, Herbst, Schreiner, and Roberts, *J. Org. Chem.*, **15**, 662 (1950).

(4) Schmidt and Zutavern, Ger. Patent **455,585** [*Chem. Abstr.*, **21**, 3057 (1927)].

(5) Houff, Ph.D. Thesis, Michigan State University, E. Lansing, Mich. (1955).

(6) V. Braun and Keller, *Ber.*, **65**, 1677 (1932).

(7) Herbst, Roberts, and Harvill, *J. Org. Chem.*, **16**, 139 (1951).