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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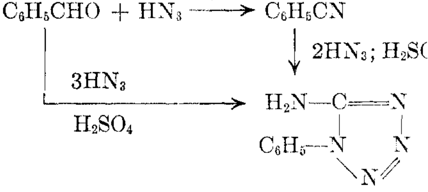
The formation of 1,5-disubstituted tetrazoles by the Schmidt reaction employing excess hydrazoic acid on ketones is well established.[1] Acetone and hydrazoic acid, for example, yield 1,5-dimethyltetrazole[2] although not in the excellent yields originally reported.[3] The action of excess hydrazoic 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).

sulfuric acid was added dropwise to a stirred solution of 10.3 g. (0.1 mole) of benzonitrile dissolved in 250 ml. of 1.0N hydrazoic acid in benzene. After an elapsed time of 3 hr. the reaction mixture was poured over 100 g. of crushed ice. The aqueous layer was neutralized with 40% sodium hydroxide solution causing the separation of a crude crystalline solid. A single recrystallization from ethanol gave 5.9 g. (37%) of 1-phenyl-5-aminotetrazole; m.p. 160.5–161.5° (reported[7] 159.5–160°).

Anal. Calcd. for $C_7H_7N_5$: N, 43.5. Found: 43.7.

1-Phenyl-5-aminotetrazole from benzaldehyde. Under reaction conditions similar to those described above, 10.6 g. (0.1 mole) of benzaldehyde dissolved in 330 ml. of 1.0 N hydrazoic acid in benzene solution was treated dropwise with 40 g. of concentrated sulfuric acid. The temperature of the reaction mixture was maintained at 35–40° for 5 hr. during which gas evolution ceased. The greenish colored reaction mixture was poured over ice and the product was isolated as described in the preceding procedure. After a single recrystallization from ethanol there was received 4.7 g. (30%) of 1-phenyl-5-aminotetrazole; m.p. 159.5–160.5°.

Anal. Calcd. for $C_7H_7N_5$: N, 43.5. Found: 43.4.

Mixtures of 1-phenyl-5-aminotetrazole prepared from benzonitrile and benzaldehyde had m.p. 160°–160.5°.

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Reaction of Silver 4-Hydroxyvalerate with Bromine

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In the course of other work in this laboratory the conversion of *cis*-2-hydroxycyclopentaneacetic acid to *cis*-2-methylcyclopentanol by way of the Hunsdiecker silver salt–bromine degradation was attempted. No carbon dioxide was evolved. Although Oldham and Ubbelohde[2] have suggested that hydroxylic compounds other than water might prevent the decarboxylation reaction from taking place, no investigation appears to have been made of the claim of Hunsdiecker, Hunsdiecker, and Vogt[3] that the reaction proceeds normally with hydroxy acids in which the hydroxyl group is not in the α- position to form hydroxyalkylhalides poorer by one C-atom.

When the reaction of methyl silver adipate with bromine,[4] which in this laboratory gave a 63% yield of methyl 5-bromovalerate, was carried out in the presence, of an equimolar quantity of cyclopentanol, little, if any, carbon dioxide was evolved and none of the desired product was obtained. The cyclopentanol contained 0.088% water; addition of three times this amount of water did not prevent decarboxylation although the yield of methyl 5-bromovalerate was only 43%. Therefore an alcoholic hydroxyl group does indeed prevent decarboxylation.

To determine what products are formed by the reaction of the silver salt of a hydroxy acid in which the hydroxyl group is not in the α- position with bromine, the reaction of silver 4-hydroxyvalerate, prepared from commercially available γ-valerolactone, was investigated. By the salt-to-bromine addition method at 0° a 36% yield of levulinic acid and a 23% yield of γ-valerolactone were obtained along with a small amount of a volatile organic acid which was not identified. No carbon dioxide was formed. By the bromine-to-salt addition method in refluxing carbon tetrachloride the yield of levulinic acid was 18% and of γ-valerolactone 46%. In addition to the small amount of volatile acid, a small quantity of a neutral material, which decomposed on distillation, was formed and a maximum of 2.5% of carbon dioxide was evolved. In both cases the remainder of the product was nonvolatile and acidic and may well have consisted largely of levulinic acid.

EXPERIMENTAL[5]

Reaction of silver 4-hydroxyvalerate with bromine. A solution of 19.8 g. (0.30 mole) of potassium hydroxide in 90 ml. of water was refluxed for one hour with 28 ml. (0.30 mole) of γ-valerolactone. The solution was then cooled and neutralized to pH 8 with a few drops of 6N nitric acid and a solution of 51.0 g. (0.30 mole) of silver nitrate in 60 ml. of water was added rapidly with stirring and cooling. After about 10 min. the silver 4-hydroxyvalerate was collected on a Büchner funnel and sucked as dry as possible. It was then washed thoroughly by trituration first with methyl alcohol and then with ether, removing the solvents by suction filtration, and dried 24 hr. at room temperature[6] in a vacuum desiccator over Drierite at <1 mm. in the dark. A 90% yield was obtained.

The silver salt (0.27 mole) was finely powdered, placed in the flask from which it was to be added, and dried another 24 hr. over phosphorus pentoxide instead of Drierite. It was then added in small portions to a stirred solution of *ca.* 16 ml. (0.31 mole) of dry[7] bromine in 150 ml. of dry[8] carbon tetrachloride cooling in an ice bath during a period of 70 min. After addition of the silver salt was complete, the reaction mixture was allowed to warm to room temperature. No carbon dioxide was detected when the flask was swept out with dry, carbon dioxide-free nitrogen, which was then passed through a weighed Ascarite tube. The silver bromide was isolated by filtration, washed thoroughly first with hot carbon tetrachloride and then with water, and air-dried; the yield was 94%.

The excess bromine was destroyed with sodium bisulfite and the carbon tetrachloride solutions were washed with an

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(1) Inquiries should be addressed to this author at 211 Scherrer St., Cranford, N. J.

(2) J. W. H. Oldham and A. R. Ubbelohde, *J. Chem. Soc.*, 368 (1941).

(3) H. Hunsdiecker, C. Hunsdiecker, and E. Vogt, U. S. Patent **2,176,181** (1939).

(4) C. F. H. Allen and C. V. Wilson, *Org. Syntheses*, **Coll. Vol. 3,** 578 (1955).

(5) Melting points were determined in open borosilicate glass capillaries using a Hershberg apparatus and are corrected unless otherwise noted.

(6) Silver 4-hydroxyvalerate darkens rapidly when heated.

(7) Bromine was dried by shaking with concentrated sulfuric acid followed by distillation from phosphorus pentoxide.

(8) Carbon tetrachloride was dried by distillation and stored over phosphorus pentoxide.