six hours. After cooling, the sirup was diluted with 200 ml. of water, at a temperature below 60°, and 85 g. of sodium nitrate in 250 ml. of water was added, at 30–42°. The temperature rose to 48°. The mixture, standing at room temperature, crystallized after one and a half hours. After eighteen hours, it was filtered, the cake washed with 100 ml. of water at 4°, and the ground, air-dried product (82 g.) extracted with ether in a Soxhlet for twenty-four hours; residue, 70 g., crystallized from 50 ml. of water 31 g. of yellow needles.

A solution of 2 g. of the crystalline yellow needles in 10 ml. of 50% sulfuric acid boiled (154°) under reflux for three hours gave no trace of 2-hydroxy-3-nitrodiphenyl even when the solution was distilled with superheated steam up to a temperature of 190° in the distilland.

(2) **VIII.**—One hundred and thirty-six grams of *o*-hydroxydiphenyl was added to 160 ml. of concd. sulfuric acid, the temperature rising from 21 to 52°. The sirup heated at 115–120° for fifteen minutes and worked up as in (1) gave 101 g. (40%) of a product which differed from that of method (1) by being soluble in six parts of hot water instead of one and by giving 14% of 2-hydroxy-3-nitrodiphenyl on addition of 50% sulfuric acid and distillation with superheated steam.

(3) The same result was obtained less tediously, as follows: thirty-four grams of *o*-hydroxydiphenyl was added to 40 ml. of concd. sulfuric acid. The temperature rose from 21 to 52°. The sirup was stirred for ten minutes, heated to 60°, and poured on 40 g. of crushed ice. The violet suspension was nitrated at 30–40° with 17 g. of sodium nitrate in 50 cc. of water. A yellow solid crystallized while the temperature rose to 47°. The mixture was filtered at 30°, the cake washed with 20 ml. of water, 50 ml. of alcohol and ether (1:1), and 50 ml. of ether, stirred for ten minutes in 200 cc. of alcohol and ether (1:1), filtered, and washed with 200 ml. of ether; 30.5 g. (48%) of yellow needles. Further extraction of a sample with ether did not remove anything. Twenty-two grams, recrystallized from six parts of water, yielded 15.2 g. of yellow needles.

Anal. Calcd. for $C_{12}H_8O_6NNaS$: C, 45.42; H, 2.52; N, 4.41; Na, 7.26; S, 10.09. Found: C, 45.43; H, 2.52; N, 4.36; Na, 7.23; S, 10.10.

Summary

1. 2-Hydroxy-3-chlorodiphenyl, m. p. 72°, and 2-hydroxy-5-chlorodiphenyl, m. p. 11°, were prepared from the corresponding amino-2-hydroxydiphenyls.
2. The structures given in the literature for the compounds of m. p. 11 and 72°, respectively, should be reversed.
3. 2-Hydroxy-3-nitrodiphenyl was prepared as a yellow steam-volatile compound.
4. Nitration of 2-hydroxy-3-chlorodiphenyl gave the colorless 2-hydroxy-5-nitro-3-chlorodiphenyl melting at 127°, which, in the literature, is erroneously listed as 2-hydroxy-3-nitro-5-chlorodiphenyl. Nitration of 2-hydroxy-5-chlorodiphenyl gave the true 2-hydroxy-3-nitro-5-chlorodiphenyl melting at 57°.
5. The "3-nitro-2-hydroxydiphenyl-5-sulfonate" which, according to the literature, gives 2-hydroxy-3-nitrodiphenyl on hydrolysis, and gives the chloronitro-2-hydroxydiphenyl melting at 127° on chlorination, appears to contain 2-hydroxy-5-nitrodiphenyl-3-sulfonate, together with a 2-hydroxy-3-nitrodiphenyl sulfonate.

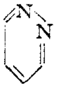
ROCHESTER 4, NEW YORK RECEIVED AUGUST 25, 1944

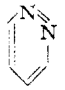
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Studies in the Pyridazine Series. The Absorption Spectrum of Pyridazine[1]

BY RICHARD CASTLEMAN EVANS AND F. Y. WISELOGLE

Studies in this Laboratory on simple compounds containing the N—N bond[2] have led to speculations concerning the modifications of such a bond when incorporated in a resonating system. An unusually interesting type of resonance is found in the aromatic nucleus of which the simplest representative is pyridazine. The pyridazine ring is unique in that the two "Lewis Structures," (A) and (B), need not have the same energy and hence need not make equal contributions in the simplified quantum mechanical representation for the state of the pyridazine molecule. It is of interest to determine whether one of the two structures may be associated predominantly with the physical properties and chemical reactions of pyridazine and simple pyridazine derivatives.


(A)


(B)

Pyridazine itself was first obtained by Ernst Täuber[3] in 1895 by the oxidation of 3,4,5,6-dibenzopyridazine to pyridazine tetracarboxylic acid and subsequent decarboxylation.

Gabriel and Colman[4,5] used hydrazine to close a ring in substituted γ-keto acids and removed the substituent groups by oxidation and decarboxylation.

Gabriel[5] obtained pyridazine in 2-g. quantities in a seven-step synthesis starting with diethyl oxalate and diethyl succinate. Condensation of these esters using sodium yielded diethyl-β-carbethoxy-α-oxoglutarate from which α-oxoglutaric acid was obtained on hydrolysis and decarboxylation. Condensation of this ketoacid with hydrazine gave 1,4,5,6-tetrahydro-6-oxopyridazine-3-carboxylic acid. Dehydrogenation with bromine followed by decarboxylation gave 3(2)-

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(1) From a dissertation submitted by R. C. Evans in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University. We are indebted to the Hynson, Westcott and Dunning Research Fund for a Grant-in-Aid covering a part of the cost of this research.

(2) Buhle, Moore and Wiselogle, THIS JOURNAL, **65**, 29 (1943).

(3) Täuber, *Ber.*, **28**, 451 (1895).

(4) Gabriel and Colman, *ibid.*, **32**, 395 (1899).

(5) Gabriel, *ibid.*, **42**, 654 (1909).

pyridazone from which 3-chloropyridazine was obtained by treatment with phosphorus oxychloride. Reduction of the chloropyridazine with fuming hydriodic acid gave pyridazine in over-all yield of 19%. We have made significant improvements in the condensation of hydrazine with α-oxoglutaric acid and in the hydrogenation of the chloropyridazine.

For the spectrographic work the pyridazine was distilled at atmospheric pressure and then fractionated at reduced pressure. The absorption spectrum of pyridazine dissolved in hexane is plotted in Fig. 1; that of pyridazine in water is plotted in Fig. 2. It will be noted that one of the absorption bands undergoes a marked shift when the character of the solvent is changed.

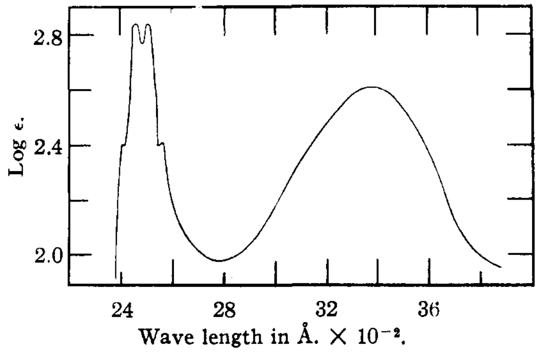

Fig. 1.—Ultraviolet absorption spectrum of pyridazine in hexane.

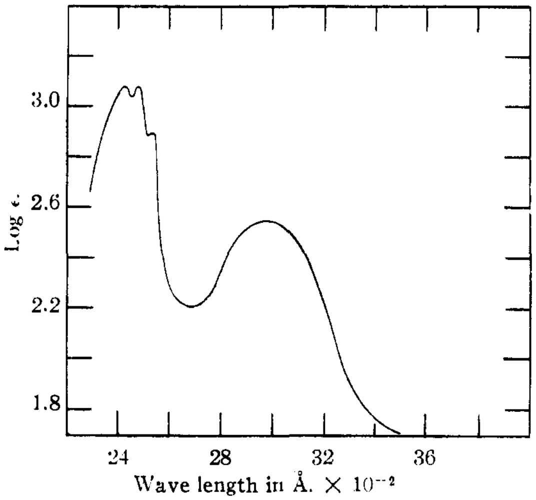

Fig. 2.—Ultraviolet absorption spectrum of pyridazine in water.

We have synthesized the isomeric 2-methyl-3(2)-pyridazone and 3-methoxypyridazine from 3(2)-pyridazone and 3-chloropyridazine respectively. Although the N-methylpyridazone is thermally stable, the methoxypyridazine, like the corresponding chloro derivative, slowly decomposes on standing at room temperature.

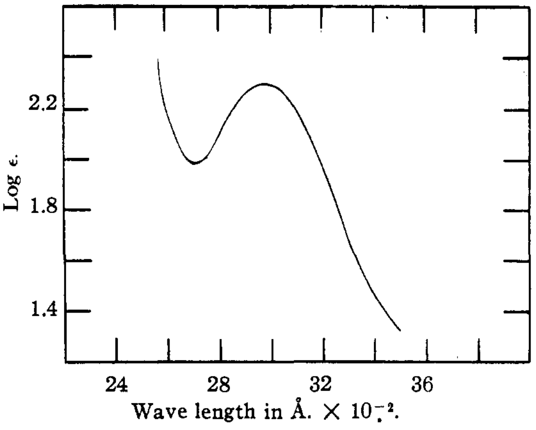

Fig. 3.—Ultraviolet absorption spectrum of pyridazine hydrochloride in water.

Experimental

1,4,5,6-Tetrahydro-6-oxopyridazine-3-carboxylic Acid.—A solution of 380 g. of α-oxoglutaric acid in 600 cc. of hot water was added slowly, with stirring, to a hot solution of 230 g. of technical sodium hydroxide and 340 g. of hydrazine sulfate in 1.5 liters of water. The heat of the reaction usually resulted in moderate boiling. The product, which precipitated from the solution on cooling, was filtered and recrystallized from 400 cc. of 2 *N* hydrochloric acid. The average yield of acid melting at 195–196° with decomposition was 180 g. (50%).

1,6-Dihydro-6-oxopyridazine-3-carboxylic Acid.—To a vigorously stirred solution of 284 g. of 1,4,5,6-tetrahydro-6-oxopyridazine-3-carboxylic acid in 1.0 liter of boiling glacial acetic acid was added 360 g. of technical bromine at a rate of several drops per second. When all of the bromine had been introduced 1.0 liter of water was added and the mixture was allowed to cool. The average yield of acid which precipitated was 182 g. (65%). The crude acid melted at 257° with decomposition.

4,5-Dihydro-3(2)-pyridazone.—Using a free flame, 100 g. of 1,4,5,6-tetrahydro-6-oxopyridazine-3-carboxylic acid was melted in a 500-cc. distilling flask with the evolution of carbon dioxide. The melt was black and viscous. When gas evolution slackened, a second batch of acid was introduced and the procedure repeated. After the decarboxylation was completed and another distilling flask had been attached as a condenser, the pressure was reduced to 6 mm. and an oil-bath used as heat source. Distillation proceeded very slowly; the product came over at about 147° and was pale red in color. Distillation was stopped when the oil-bath reached 220°. The product was distilled twice from a small apparatus of the same type, coming over at 94° at 3 mm. The condensed liquid, which was viscous and water-clear, slowly crystallized upon cooling. The average yield was 32 g. (23%), m. p. 41–3°.[6]

Anal. Calcd. for $C_4H_6N_2O$: C, 49.0; H, 6.2. Found: C, 48.0, 48.9; H, 6.0, 6.0.

3(2)-Pyridazone.—Three batches of 100 g. of 1,6-dihydro-6-oxopyridazine-3-carboxylic acid each were decarboxylated by melting at ordinary pressure with a free flame. After the evolution of carbon dioxide had subsided, the pressure was reduced to 2–3 mm. and the rather thin, dark colored 3(2)-pyridazone was distilled, using an oil-bath for heating. It came over at 160–170°, pale yellow in color. The product was redistilled in an all-glass Claisen sublimation apparatus but still came over pale yellow, this time at 146–148° at 1 mm. The average yield was 185 g. (90%), m. p. 102°.

3-Chloropyridazine.—To 30 g. of 3(2)-pyridazone in a 200-cc. balloon flask was added, with continuous stirring,

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(6) Carrière, *Ann. chim.*, **17**, 38 (1922).

25 cc. of phosphorus oxychloride. After the reaction had moderated, within twenty minutes, an additional 25-cc. portion of phosphorus oxychloride was added. The mixture was stirred for an additional forty-five minutes and was maintained during this time at a temperature of 65–75°. The mixture was then cooled and poured into 50 cc. of cold water. After neutralizing the solution with sodium carbonate, the mixture was repeatedly extracted with ether until the organic layer was nearly colorless. The ether solution was filtered and the ether was removed at room temperature. The residual oily 3-chloropyridazine was used for the hydrogenation reactions without purification. The average yield was 24 g. (68%).

For purification the product was distilled at 1 mm. pressure. If the bath temperature rose to about 95°, however, the chloropyridazine decomposed rapidly, liberating a large amount of gas and leaving a carbonaceous residue in the distilling flask. The colorless distillate solidified in the well-cooled receiver but the product could not be kept for more than a few hours without extensive decomposition. Solutions of 3-chloropyridazine in alcohol appear to be relatively stable at room temperature.

Pyridazine.—A mixture of 24 g. of 3-chloropyridazine, 20 cc. of concentrated ammonia water, 50 cc. of 95% alcohol, and 0.75 g. of a palladium[7] catalyst was hydrogenated at room temperature and under an initial pressure of 45 lb. The reaction was essentially complete within fifteen to thirty minutes. The filtrate was evaporated to 70 cc. and was treated with strong aqueous sodium hydroxide. The aqueous solution was extracted four to five times with benzene. The benzene solution was dried over solid potassium hydroxide and the benzene was removed. The pyridazine distilled at 62–67° under 2–3 mm. pressure. The average yield was 5.2 g. For the spectrographic work the pyridazine was distilled at atmospheric pressure, boiling at 205–206°, and then fractionated at 1 mm. pressure, the product distilling at 47–48°. The following physical constants were determined on the spectrographic sample: d^{20}_{20}, 1.111; n^{30}_{D}, 1.5148.

The surprisingly high boiling point of pyridazine suggested the possibility that association might be detected in solution. However, a solution of 0.2137 g. of pyridazine in 23.577 g. of benzene resulted in a freezing point lowering of 0.55°, giving an observed molecular weight of 84.5 as against a calculated value of 80.0.

2-Methyl-3(2)-pyridazone.—To a mixture of 15 g. of 3(2)-pyridazone and 10 g. of methyl sulfate in 50 cc. of methanol was added, with shaking, a solution of 8 g. of sodium hydroxide in water. After one hour of refluxing the alcohol was removed and the residue was extracted with benzene. Distillation of the residue from the benzene extract at 1–2 mm. gave 2.0 g. of a hygroscopic oil which readily crystallized to a hygroscopic solid melting at 38–39°.

Anal. Calcd. for $C_5H_6N_2O$: C, 54.5; H, 5.5. Found: C, 55.0; H, 5.5.

3-Methoxypyridazine.—To a methyl alcohol solution of 12 g. of 3-chloropyridazine was added a solution made up by dissolving 3.7 g. of sodium in 40 cc. of methanol. The temperature rose to about 50° and the mixture was heated under a reflux condenser for two hours. After removal of the methanol the residue was treated with a few cc. of strong aqueous sodium hydroxide solution and extracted with benzene until the extract was colorless. The benzene solution was dried with calcium chloride, filtered, and the benzene was removed. The residue distilled at 77–78° at 5 mm. The average yield was 6.0 g. (55%), n^{30}_{D} 1.5086.

Anal. Calcd. for $C_6H_6N_2O$: C, 54.5; H, 5.5. Found: C, 54.3; H, 5.2, 5.4.

3-Ethoxypyridazine.—3-Ethoxypyridazine was obtained in 56% yield under similar conditions. The product distilled at 69–71° at 2–3 mm. and the solid melted at 35–36°. The refractive index of the liquid at 30° was 1.5000.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.0; H, 6.5. Found: C, 58.2; H, 6.4.

This compound was also prepared by the reaction of 3-chloropyridazine with a solution of potassium hydroxide in 95% ethyl alcohol.

Summary

The absorption spectrum of pyridazine solutions in hexane and water from 2400 to 3800 Å. is reproduced.

Three new pyridazine derivatives have been prepared. They are 2-methyl-3(2)-pyridazone, 3-methoxypyridazine and 3-ethoxypyridazine.

BALTIMORE, MD. RECEIVED MARCH 13, 1944

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(7) We are indebted to Dr. Walter H. Hartung of the University of Maryland for allowing us to report the method of preparation of this catalyst prior to his publication. It was prepared by hydrogenating for thirty minutes under an initial pressure of 45 lb. a mixture composed of 16.4 g. of sodium acetate, 3.0 g. of Norit A, and 3 cc. of a 10% solution of palladium chloride. The Norit was then filtered, washed with water, and dried in a stream of nitrogen at 70°. This catalyst is pyrophoric in the presence of alcohol.

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

The Sorption of Hydrogen by Poisoned Copper. Temperature Variation Experiments

BY CARROLL W. GRIFFIN

Introduction

The effect of a small amount of carbon monoxide both upon the catalytic activity of massive copper in the hydrogenation of ethylene[1] and upon the sorption of hydrogen by this metal[2] has been established. Whereas the catalytic activity is almost completely destroyed by the poison, the 0° sorption of hydrogen is actually increased at low pressures although decreased at high pressures. Interpreting these results, the author suggested that not only physical and activated adsorption of hydrogen occurs upon copper, but, in addition, solution of hydrogen. The same conclusion was reached by Benton and White.[3] Numerous experiments have been carried out to throw further light upon this question of solubility. These have included sorption measurements with supported sorbents which could have very little accommodation for solution[4] and "experiments with temperature variation," introduced by Benton and White[3] with massive copper and extended by the writer to include supported metals.[5] These data support the belief that many

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(1) Pease and Stewart, THIS JOURNAL, **47**, 1235 (1925).

(2) Griffin, *ibid.*, **49**, 2136 (1927).

(3) Benton and White, *ibid.*, **54**, 1373 (1932).

(4) Griffin, *ibid.*, **57**, 1206 (1935); **59**, 2431 (1937).

(5) Griffin, *ibid.*, **61**, 270 (1939); **63**, 2957 (1941).