An attempt was also made to establish the constitution of tyrosine-3-sulfonic acid by conversion into a cinnamic acid derivative through deaminization by digestion with methyl iodide and potassium hydroxide. This transformation is not accomplished without complete degradation of the greater part of the sulfonic acid. We did succeed in obtaining a small quantity of the desired cinnamic acid derivative, $HO_3S(OH)C_6H_3CH = CHCOOH$ in the form of its potassium salt, but the quantity formed was so small that this method of operating proved of no practical utility. This potassium salt was purified by crystallization from water. It reacted with concentrated sulfuric acid to give a red colored solution, but did not give color reactions when treated with ferric chloride solution or Millon's reagent. It had no definite melting point.

Anal. Calcd. for $C_{10}H_9O_6SK$: S, 10.80. Found: S, 10.66, 10.9.

Summary

1. When tyrosine is allowed to react with sulfuric acid at 95–100° it is converted smoothly into tyrosine-3-sulfonic acid.

2. The structure of this acid is established by the fact that it is converted into 3,5-dinitrotyrosine by the action of nitric acid.
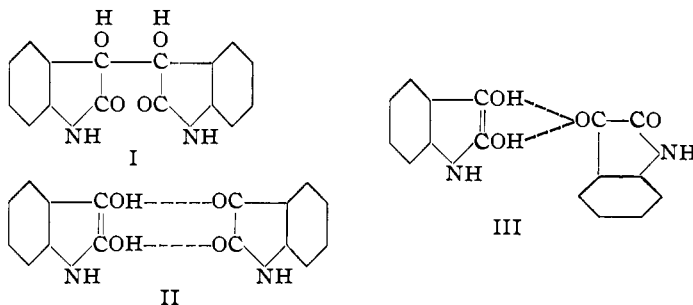
NEW HAVEN, CONNECTICUT

SOME OBSERVATIONS CONCERNING THE STRUCTURE OF ISATIDE

BY WARD C. SUMPTER

The isatin pinacol formula for isatide, I, proposed by Kohn[1] and by Lefèvre,[2] has been disputed by Heller.[3] Heller regards isatide as being a quinhydrone type of compound, II or III.

Isatide is best prepared by condensing isatin with dioxindole in alcoholic solution in the presence of piperidine. The condensation of a substituted dioxindole with isatin and of a substituted isatin with dioxindole should give rise to two different isatides if the quinhydrone formulation is correct.

[1] Kohn, *Ber.*, **49**, 2514 (1916); Kohn and Klein, *Monatsh.*, **33**, 929 (1912); Kohn and Ostersetzer, *ibid.*, **37**, 25 (1916).

[2] Lefèvre, *Bull. soc. chim.*, **19**, 113 (1916).

[3] Heller, *Ber.*, **49**, 1406 (1916); Heller and Lauth, *ibid.*, **62**, 343 (1929).

Wahl and Faivret[4] obtained a 5-methylisatide by condensing dioxindole with 5-methylisatin. The condensation of 5-methyldioxindole with isatin gives the same 5-methylisatide. This fact precludes acceptance of the quinhydrone formulation and strongly supports the symmetrical isatin pinacol formula.

Experimental

5-Methylisatide. A. From 5-methylisatin and dioxindole, Method of Wahl and Faivret.—Ten drops of piperidine was added to a solution of 1.9 g. of dioxindole and 2 g. of 5-methylisatin in 50 cc. of 95% ethyl alcohol and the whole heated on the water-bath under a reflux condenser for one hour. After cooling the precipitate was filtered off and washed repeatedly with small portions of alcohol. The straw colored powder so obtained could not be crystallized from any of the usual organic solvents. The yield was 3.1 g. or 81% of the theoretical. The substance softened at about 220° and melted with decomposition at 228–230°. Wahl and Faivret reported 229–230°.

B. From Isatin and 5-Methyldioxindole.—The procedure was identical with that described above. The substance softened at about 220° and melted with decomposition at 227–230°. A mixture of this substance with the 5-methylisatide prepared from dioxindole and 5-methylisatin melted with decomposition at 227–230°. The yield was 3 g. or 79% of the theoretical.

The writer is indebted to the Dow Chemical Co. for the gift of a generous supply of indigo from which the isatin and dioxindole used in this work were prepared.

Summary

The condensation of 5-methyldioxindole with isatin yields the same 5-methylisatide obtained by Wahl and Faivret from 5-methylisatin and dioxindole. In the light of this fact the unsymmetrical quinhydrone formulation for isatide is untenable. The isatin pinacol formula is probably correct.

[4] Wahl and Faivret, *Ann. chim.*, 5, 314 (1926).

CLARKSVILLE, ARKANSAS

THE NUMBER OF STRUCTURAL ISOMERS OF CERTAIN HOMOLOGS OF METHANE AND METHANOL

BY DOUGLASS PERRY

A very ingenious general method for determining the number of structurally isomeric paraffin hydrocarbons has been published recently.[1] The purpose of this article is to extend the results previously given by applying this method to the computation of the number of structural isomers of hydrocarbons of the methane series of carbon contents ranging from twenty to forty, inclusive, and of hexacontane.

In order to calculate the number of structural isomers of a given paraffin hydrocarbon by the method referred to above, it is first necessary to know

[1] Henze and Blair, THIS JOURNAL, **53**, 3077 (1931).