Proceedings of the Iowa Academy of Science

Volume 40 | Annual Issue Article 54

1933

Steric Hindrance as a Factor in the Hydrolytic Stability of Aromatic Ketimines

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STERIC HINDRANCE AS A FACTOR IN THE HYDROLYTIC STABILITY OF AROMATIC KETIMINES

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A comparison of the velocities of hydrolysis of the 2-, the 3- and the 4-methyl diphenyl ketimine hydrochlorides, in which the velocity of the first is very much slower than either of the other two, suggests steric hindrance. The very slow rate of hydrolysis of 2, 4, 6-trihydroxy diphenyl ketimine hydrochloride has been reported by one of us. This slow rate may be accounted for on the basis of the multiple opportunities for tautomerism involving the very stable enamine forms. We have recently found 2-methyl, 4, 6-dihydroxy diphenyl (orcinyl phenyl) ketimine hydrochloride to be even more slowly hydrolyzed. It would appear here that the steric hindrance effect outweighs the possible enamine tautomerism.

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THE DETERMINATION OF MANGANESE IN BIOLOGICAL MATERIAL

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One of the best methods for the determination of manganese in very small amounts in biological material is the adaptation of Willard's oxidation of the Mn in acid solution by KIO_4, and a comparison in Nessler tubes of the color produced, with a known standard similarly treated. Skinner and Peterson showed that if animal tissue was ashed in a muffle furnace and extracted with H_2PO_4, the KIO_4 oxidized the Mn in the solution without loss of color. They found 0.01 mg Mn in 50 cc. solution gave a readable color in Nessler tubes against an inverted V of white paper.

In applying this method to the determination of manganese in the salts for nutrient solutions, ashing was not needed unless organic substances were present. It was found possible, by oxidizing with KIO_4 together with 5 cc. of 85 per cent H_3PO_4 in a 50 cc. solution, when a frame with a milk glass was used and the light from the north sky, in almost all cases to determine the presence of 0.001 mg Mn; increases of 0.001 mg could be checked. The color of the oxidized solution was very stable. The procedure, after ashing the solid, was very successful for Mn in iron citrate.