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Thiochrome: A Convenient Synthesis from Thiamine[1]

Although the synthesis of thiochrome is readily attained by either the oxidation of thiamine by alkaline potassium ferricyanide[2] or the thermal decomposition of thiamine disulfide[3], its isolation from these procedures is inconvenient.

Studies by METZLER and MAIER[4] on the reactions of base with thiamine have disclosed that a tricyclic form of thiamine can be isolated in absolute alcohol. This study and also the observation by WOSTMANN and KNIGHT[5] that potassium ferricyanide in the presence of methyl alcohol favors a higher conversion of thiamine to thiochrome led us to attempt a simple oxidation of the vitamin in absolute methanol. The best oxidation procedure is as follows: Thiamine (1.68 g, 0.005 m) is suspended in absolute methyl alcohol (50 cm³). Iodine (1.27 g, 0.005 m) is then added and the mixture is stirred until all of the iodine has dissolved. At this point, potassium carbonate (4.14 g, 0.03 m) is added, and the mixture is stirred for 30 min. By this time the iodine color has discharged, and the bright yellow solution is then filtered to remove unreacted carbonate and potassium iodide. After filtration the solution is neutralized by the addition of acetic acid. On concentrating the filtrate at room temperature, crystals of thiochrome (0.265 g) (λ_{max} (EtOH) = 375; log ε = 4.20) are deposited. The melting point of the crude product ranges from 220–224°. The product was purified by recrystallization from chloroform. On further concentration of the filtrate, thiamine disulfide (0.138 g) (λ_{max} (EtOH) = 235, 275; log ε = 4.15, 3.80) was also isolated. The reaction time and neutralization step are critical. When the reaction time was lengthened to 1 h, it was found that the major products were thiazolone and disulfide. Similar results were also noted when the reaction mixture was concentrated without neutralizing the excess base. The oxidizing agents, nitrobenzene and nitrosobenzene, can also be substituted for iodine in the reaction. Under these conditions, the oxidizing agents are converted to azoxybenzene; thiamine is converted to thiochrome and disulfide.

Zusammenfassung. Die Arbeit gibt eine chemische Beschreibung des Präparates Thiochrom.

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Department of Biochemistry, Louisiana State University, Baton Rouge (Louisiana USA), January 11, 1965.

[1] This investigation was supported in part by Public Health Service Research Grant AM-08590-1 from the Arthritis and Metabolic Diseases Program.

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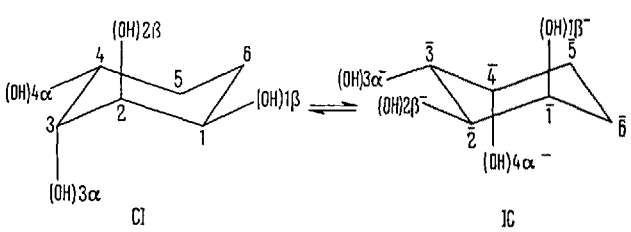
Molecular Rotations of Polyhydroxycyclohexanes in Relation to their Structures[1]

(–)-1,2/3,4-Cyclohexanetetrol

By applying the PM-method[2], the molecular rotation of (–)-1,2/3,4-cyclohexanetetrol is to be considered. The polyhydroxycyclohexanes and their observed molecular rotations are listed in Table I.

As is apparent in the Figure, (–)-1,2/3,4-cyclohexanetetrol has always two axial OH groups (which are *trans* to each other) and two equatorial OH groups (which are also *trans* to each other) in both the C 1- and 1 C-conformations. Therefore, the energy due to the interactions between four OH groups and the cyclohexane ring (including its H atoms) may be nearly equal in the two conformations. The number of intramolecular hydrogen bonds is, however, different. Concretely speaking, there are two adjacent *cis* hydrogen bonds in C 1 conformation (one is between $(OH)^{1\beta}$ and $(OH)^{2\beta}$ and the other is between $(OH)^{3\alpha}$ and $(OH)^{4\alpha}$). On the other hand, in 1 C conformation, there are two adjacent *cis* hydrogen bonds (one is between $(OH)^{1\beta-}$ and $(OH)^{2\beta-}$ and the other is between $(OH)^{3\alpha-}$ and $(OH)^{4\alpha-}$) and moreover there is one *trans* hydrogen bond (between $(OH)^{2\beta-}$ and $(OH)^{3\alpha-}$). Therefore it can be presumed that this *trans* hydrogen bond makes the 1 C conformation more stable than the C 1 conformation. In the equilibrium C 1 $\rightleftarrows$ 1 C, accordingly, the concentration of the 1 C conformation, [1 C],



C1 1C

[1] Part III. Part II, see S. YAMANA, Bull. chem. Soc. Japan *34*, 1212 (1961).

[2] S. YAMANA, J. Am. chem. Soc. *86*, 1606 (1964).