THIAMIN YLIDE: ISOLATION AND ITS CHEMICAL BEHAVIOR

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The reaction of thiamin monochloride with an equivalent of NaOEt in EtOH gave a neutral compound; mp 127-129°C; Anal. $C_{12}H_{16}N_4OS \cdot 1/5H_2O$; UV λ_{max} (EtOH) nm (log ε) 236 (4.08), 270 (3.81).

Spectroscopic data indicated that the compound is thiamin ylide 1. This was further supported by its chemical behavior. p-Nitrobenzoic acid or p-nitrothiophenol served as a proton donor to 1, giving thiamin salt. Treatment with excess EtONa in EtOH yielded the yellow form of thiamin. These finding clearly demonstrates the role of 1 as an intermediate in the conversion of thiamin into thiamin thiolate as well as in H-D exchange of C2 proton of thiamine.

Acyloin condensation of 2-furaldehyde was catalyzed by 1 under very mild and neutral conditions. Aryldisulfide also reacted with 1 under neutral condition to give a mixture of thiochrome and SB_1. These behaviors of 1 are entirely consistent with those of in situ generated thiamin ylide.

This is the first example of the identification of thiamin ylide which was proposed by R. Breslow in 1957 as the most important intermediate in the thiamin chemistry.