RECYCLIZATION OF MESOIONIC 4,5-DIPHENYL-1,3,4-THIADIAZOLE-2-THIONE

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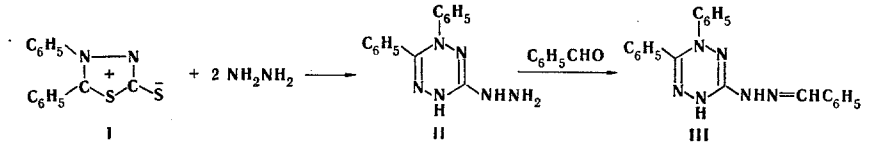
Recyclization reactions of mesoionic thiadiazoles have not been described in the literature. When mesoionic 4,5-diphenyl-1,3,4-thiadiazole-2-thione (I) is refluxed in dioxane with a fivefold molar excess of hydrazine hydrate, it undergoes recyclization to give 1,6-diphenyl-3-hydrazino-1,4-dihydro-1,2,4,5-tetrazine (II) with mp 157-158° (successively from aqueous alcohol and benzene) in 74% yield. UV spectrum, λ_{max} (methanol): 356 and 254 nm (log ε 3.26 and 4.26). IR spectrum (in KBr): 3290, 3260, 1650, and 1580 cm^{-1}. The mass spectrum of II contains an intense molecular ion peak at m/e 266 (90%) and the following fragment peaks: 251 (6), 236 (31), 221 (6), 196 (15), 195 (10), 181 (15), 180 (83), 104 (30), 103 (28), 93 (27), 78 (33), 77 (100), 74 (21). Hydrogen sulfide evolution was observed during the reaction.



I II III

The yellow crystals of II give a colorless solution in 10% hydrochloric acid and are reisolated when the solution is made alkaline. Hydrazone III, with mp 211.5-212°, was obtained in quantitative yield when II was heated with benzaldehyde in a mixture of glacial acetic acid and anhydrous sodium acetate. UV spectrum, λ_{max} (methanol) 280 nm (log ε 4.43). IR spectrum (KBr pellet): 3330, 1640, and 1580 cm^{-1}. Mass spectrum: [M^+] 354 (15), 236 (20), 197 (12), 196 (85), 195 (41), 180 (54), 160 (78), 119 (12), 118 (19), 93 (62), 91 (24), 77 (100), 76 (20).

The results of elementary analysis of II and III were in agreement with the calculated values.

The proposed synthetic method may be a rather simple method for the preparation of functional derivatives of 1,4-dihydro-1,2,4,5-tetrazine.

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