TRANSFORMATIONS OF 2-CYCLOALKYLIMINO-6H-1,3,4-THIADIAZINES UNDER UV-IRRADIATION

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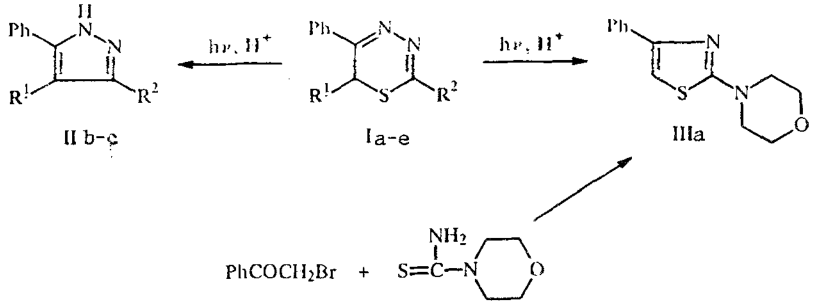
It is known that 1,3,4-thiadiazines are transformed in acidic and basic media to form pyrazoles or mercaptopyrazoles [1, 2]. We showed earlier that upon stirring a solution of thiadiazines Ia-e in dilute mineral acids only Ia and Ib (R^2 = morpholine) are observed to react [3]. Other analogs were stable under these conditions.

We discovered that upon irradiation of solutions of the thiadiazines Ib-e in 0.1 N HBr with UV light (λ 309 nm, N 1 kW), all thiadiazines react at room temperature to form the pyrazoles IIb-e and sulfur. Complete conversion takes place over 2-6 h, depending upon the character of the substituent R^2.



I-IIIa) R^1 = H, R^2 = morpholine; b) R^1 = C_2H_5, R^2 = morpholine; c) R^1 = H, R^2 = piperidine; d) R^1 = H, R^2 = pyrrolidine; e) R^1 = H, R^2 = hexamethyleneimine

Transformation of 2-morpholino-5-phenyl-6H-1,3,4-thiadiazine Ia proceeded differently. UV-radiation produced 2-morpholino-5-phenylthiazole (IIIa) by elimination of nitrogen (λ_{max} 272 nm, pK_a 3.23, R_f 0.84 in the system butanol–CH_3COOH–H_2O, 4:1:5). Its 6-ethyl-substituted analog Ib gave 3-morpholino-5-phenylpyrazole IIb under these same conditions.

The structures of the conversion products were established with the help of our synthesized standards of IIb-e and IIIa. The UV spectra, ionization constants, and R_f values obtained after irradiation of solutions were identical to the corresponding parameters of the standard compounds.

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