1,5-DIPOLAR CYCLIZATION OF 2-DIAZO-2-CYANOACETIC ACID DERIVATIVES TO 1,2,3-TRIAZOLES AND 1,2,3-THIADIAZOLES

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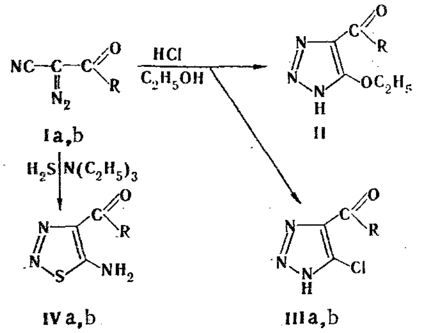
Reactions involving the electrocyclization of α-diazo nitriles to 1,2,3-triazoles have not been described in the literature. We have observed that diazocyanoacetic acid derivatives Ia, b [1] react with hydrogen chloride in ethanol to give 1,2,3-triazoles. However, instead of the expected ethoxytriazoles II, we isolated compounds that we identified as 5-chloro-1H-1,2,3-triazole-4-carboxylic acid derivatives on the basis of the results of elementary analysis and data from the PMR, IR, and UV spectra. Compound IIIa had mp 192-194°C (from water). IR spectrum (KBr): 3485 (NH) and 1683 cm^{-1} (C=O). UV spectrum (in water) λ_{max} (log ε): 231 (3.84). Compound IIIb had mp 74-77°C (from water). IR spectrum (KBr): 1690 cm^{-1} (C=O). UV spectrum (in water), λ_{max} (log ε): 237 nm (4.08). PMR spectrum (CD_3OD): 4.47 (2H, q, J = 7.2 Hz) and 1.39 ppm (3H, t, J = 7.2 Hz). The same cyclization products were obtained when chloroform was used as the solvent.



I, III, IV a R=NH_2; b R=OC_2H_5

Diazo compounds Ia, b also react with hydrogen sulfide. However, the electrocyclization that follows the addition of hydrogen sulfide to the cyano group proceeds via a different pathway to give 5-amino-1,2,3-thiadiazole-4-carboxylic acid derivatives. Compound IVa had mp 178-179°C (from water). IR spectrum (KBr): 3375 (NH) and 1677 cm^{-1} (C=O). UV spectrum (in water), λ_{max} (log ε): 260 (3.99) and 291 nm (3.89). Compound IVb had mp 125-126°C (from water). IR spectrum (KBr): 3240, 3350 (NH_2); 1690 cm^{-1} (C=O). UV spectrum (in water), λ_{max} (log ε): 225 (sh, 3.45), 262 (3.90), and 284 nm (sh, 3.78). PMR spectrum (d_6-DMSO): 8.40 (2H, q, J = 7.8 Hz) and 1.36 ppm (3H, t, J = 7.8 Hz, CH_3). Compound IVb was identical to the compound previously obtained [2] from diazoacetic ester.

The individuality of the compounds obtained was confirmed by means of thin-layer chromatography.

LITERATURE CITED

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