

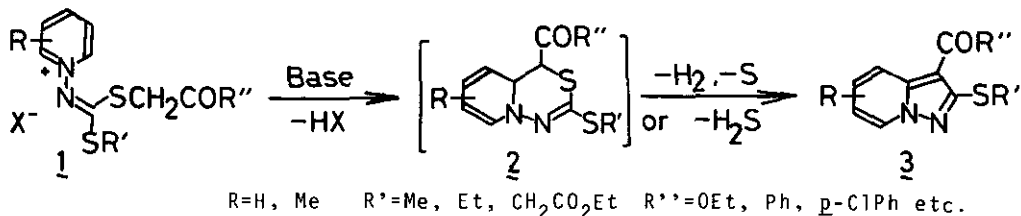
ABNORMAL FORMATION OF PYRAZOLO[1,5-a]PYRIDINES VIA THE
DESULFURIZATION OF PYRIDO[1,2-b]-4,1,2-THIADIAZINE INTERMEDIATES

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In the course of our investigation for preparing some nitrogen-bridged heterocycles such as indolizines and pyrazolo[1,5-a]pyridines, we have recently described some convenient synthetic methods for these heterocycles. In particular, compounds, thus obtained, were appropriately functionalized, and their versatility as precursors for further condensed heterocycles were also indicated.¹⁻⁴⁾ This report provides the results and discussion on a novel and unusual synthetic method for functionalized pyrazolo[1,5-a]pyridine derivatives by the alkaline treatment of pyridinium salts possessing an isocyanate dithioacetal group at the 1-position.

In order to introduce a substituent involving an active methylene group onto the 2-position of pyrazolo[1,5-a]pyridine, when the reactions of pyridinium salts **1** with various reagents in the presence of alkali were carried out, the initially expected products could not be obtained at all. However, the unexpected intramolecular cyclization products, 3-acyl-2-alkylthiopyrazolo[1,5-a]pyridines **3**, were formed directly in considerable yields. The generality and the wide applicability of this reaction were proved immediately by the uses of various pyridinium salts **1**. Mechanistically, it is clear that pyrido[1,2-b]-4,1,2-thiadiazine intermediates **2** must be involved in this reaction, and our attempts to detect such intriguing molecules will be also discussed.



References

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