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THE SYNTHESIS OF THIENO[3,2-e]PYRAZOLO[4,3-c]PYRIDINE. A NEW HETEROCYCLIC SYSTEM.

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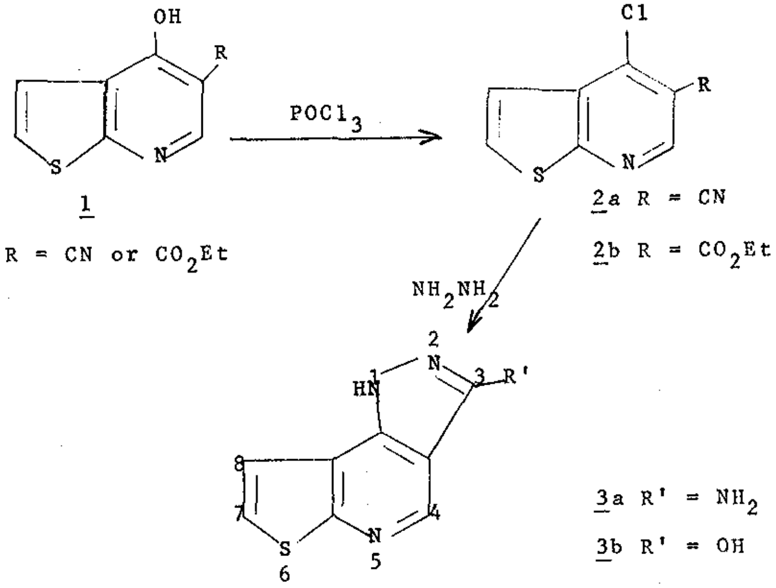
The synthesis of the title heterocyclic system from appropriate thieno[2,3-b]pyridine is reported.

During the course of our work on the synthesis of analogs of nalidixic acid, we had obtained various 4-hydroxythieno[2,3-b]-pyridines containing substituents such as cyano and carbethoxy in the 5 position (1). Appropriate modifications of these groups and further reactions could lead to other heterocyclic systems such as a new heterocyclic system - thieno[3,2-e]pyrazolo[4,3-c]pyridine (3).

The synthesis of this system is presented in the following scheme:



1 could easily be converted to the corresponding 2 by heating under reflux with an excess of phosphoryl chloride over a period of two hours and thus 5-substituted 4-chlorothieno[2,3-b]pyridines (2a, mp 120° and 2b, mp 69-70°)were isolated from these reactions in 76% yield. When 2a was heated under reflux with hydrazine hydrate for a period of eight hours, 3-aminothieno[3,2-e]pyrazolo[4,3-c]pyridine (3a), mp >300° was isolated in 85% yield. It was recrystallized from a mixture of dimethyl sulfoxide and water. ir ν_{max}^{KBr} : 3260, 3220 and 3100 cm^{-1} (NH_2 and NH). nmr (DMSO-d_6, δ): 8.92 (s, 1H, C_4H); 7.75 (d, 1H, J = 6 Hz, C_7H); 7.55 (d, 1H, J = 6 Hz, C_8H). A similar treatment of 2b with hydrazine hydrate gave 3-hydroxythieno[3,2-e]pyrazolo[4,3-c]pyridine (3b) in 80% yield, mp >300° (dimethyl sulfoxide-water). ir ν_{max}^{KBr} : 3350 and 2980 cm^{-1} (OH and NH). nmr (DMSO-d_6, δ) : 8.86 (s, 1H, C_4H); 7.81 (d, 1H,

J = 6 Hz, C_7H); 7.62 (d, 1H, J = 6 Hz, C_8H); 8.26 (s, exchangeable hydrogen). The charecteristic absorptions due to the cyano and carbethoxy groups in 2a and 2b, respectively, were absent in the ir spectra of 3a and 3b. Both the 3a and 3b gave satisfactory elemental analyses.

REFERENCES

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