

A NEW TETRACYCLIC HETEROAROMATIC RING SYSTEM -

THIENO[3",2":5',6']PYRIDO[3',4':4,3]PYRAZOLO[1,5-a]PYRIMIDINE

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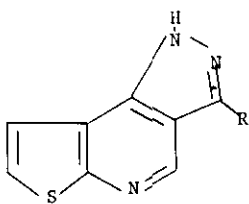
The title ring system was obtained from the condensation of 3-aminothieno[3,2-e]pyrazolo[4,3-c]pyridine with the appropriate reagents.

In a previous publication¹ we had reported the synthesis of a new tricyclic ring system- thieno[3,2-e]pyrazolo[4,3-c]pyridine (Ia). During our further work on this system the 3-amino derivative (Ib) was subjected to various reactions in order to obtain other derivatives of I. We would like to report the synthesis of a new tetracyclic heteroaromatic ring system containing four different heterocyclic rings that was isolated in the course of our investigations.

When an equimolar mixture of Ib and 1,1,3,3-tetraethoxypropane in ethanol containing anhydrous zinc chloride and a few drops of hydrochloric acid was made to reflux for an hour there was obtained thieno[3",2":5',6']pyrido[3',4':4,3]-pyrazolo[1,5-a]pyrimidine (IIa) in 76.5% yield. It was crystallized from ethanol as beige colored needles mp 270-271°. pmr (DMSO-d₆, temp. 125°, δ): 9.52 (dd, 1H, J_{7,8}=4.5 and J_{7,9}=1.9 Hz, C₇H); 9.40 (s, 1H, C₅H); 8.94 (dd, 1H, J_{8,9}=7.0 and J_{7,9}=1.9 Hz, C₉H); 7.87 (s, 2H, C₁H and C₂H); and 7.61 (dd, 1H, J_{7,8}=4.5 and J_{8,9}=7.0 Hz, C₈H). ms m/e: 226(M⁺). The ir spectrum of IIa lacked the characteristic peaks due to the amino group of Ib.

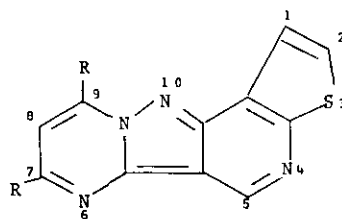
Other reactions of Ib with the appropriate reagents such as 1,3-dicarbonyl compounds may lead to yet other derivatives of the title ring system. Thus the condensation of Ib with 2,4-pentanedione in ethanol in the presence of zinc chloride and hydrochloric acid gave IIb, mp 231-232° (ethanol). yield 93.2%. pmr (CF₃CO₂H, δ): 9.95 (s, 1H, C₅H); 8.15 (d, 1H, J_{1,2}=6.0 Hz, C₁H); 7.98 (d, 1H, J_{1,2}=6.0 Hz, C₂H); 7.76 (s, 1H, C₈H); 3.28 and 3.09 (2s, 6H, C₇Me and C₉Me). ms m/e: 254(M⁺). Both the new products IIa and IIb gave satisfactory elemental analyses.

The synthesis of other derivatives of II and their reactions are currently under investigations.



Ia R=H

Ib R=NH₂



IIa R=H

IIb R=Me

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REFERENCES

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