

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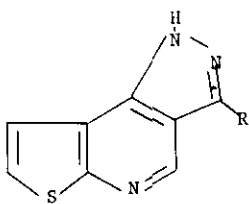
The title ring system was obtained from the condensation of 3-aminothieno[3,2-e]pyrazolo[4,3-c]pyridine with the appropriate reagents.

In a previous publication<sup>1</sup> 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-d<sub>6</sub>, temp. 125°, δ): 9.52 (dd, 1H, J<sub>7,8</sub>=4.5 and J<sub>7,9</sub>=1.9 Hz, C<sub>7</sub>H); 9.40 (s, 1H, C<sub>5</sub>H); 8.94 (dd, 1H, J<sub>8,9</sub>=7.0 and J<sub>7,9</sub>=1.9 Hz, C<sub>9</sub>H); 7.87 (s, 2H, C<sub>1</sub>H and C<sub>2</sub>H); and 7.61 (dd, 1H, J<sub>7,8</sub>=4.5 and J<sub>8,9</sub>=7.0 Hz, C<sub>8</sub>H). ms m/e: 226(M<sup>+</sup>). The ir spectrum of IIa lacked the characteristic peaks due to the amino group of Ib.

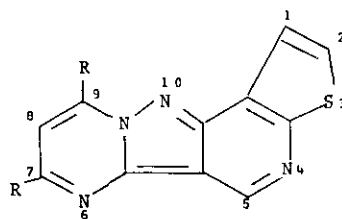
Other reactions of Ib with the appropriate reagents such as 1,3-dicarbonyl compounds may lead to yet other derivatives of the title ring system. Thus the condensation of Ib with 2,4-pentanedione in ethanol in the presence of zinc chloride and hydrochloric acid gave IIb, mp 231-232° (ethanol). yield 93.2%. pmr (CF<sub>3</sub>CO<sub>2</sub>H, δ): 9.95 (s, 1H, C<sub>5</sub>H); 8.15 (d, 1H, J<sub>1,2</sub>=6.0 Hz, C<sub>1</sub>H); 7.98 (d, 1H, J<sub>1,2</sub>=6.0 Hz, C<sub>2</sub>H); 7.76 (s, 1H, C<sub>8</sub>H); 3.28 and 3.09 (2s, 6H, C<sub>7</sub>Me and C<sub>9</sub>Me). ms m/e: 254(M<sup>+</sup>). 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=NH<sub>2</sub>



IIa R=H

IIb R=Me

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#### REFERENCES

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