PREPARATION OF FUSED MESO-IONIC COMPOUNDS FROM 1-AMINO-4,6-DIPHENYL-2-PYRIDONE

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Summary : A number of meso-ionic compounds derivatives of the bicyclic system 1,3,4-oxadiazolo[3,2-a] pyridine have been prepared from 1-amino-4,6-diphenyl-2-pyridone, either by thermal way or via iminophosphorane (4)

A variety of monocyclic meso-ionic compounds are known<sup>1</sup>, but derivatives containing fused meso-ionic rings are less common, especially those with the second ring heteroaromatic<sup>2</sup>. We report attempts to synthesize 1,3,4-oxadiazolo-[3,2-a] pyridinium-2-olate, 2-thiolate and 2-aminides by two approaches : (a) by thermal route, and (b) <u>via</u> iminophosphorane (<u>4</u>).

a) Thermal route.

1-Amino-4,6-diphenyl-2-pyridone (1) reacts with phenyl and  $\ll$ -naphthylisocyanate in dimethylformamide at room temperature to yield the corresponding NN'-disubstituted ureas (2) in high yield (88-95%). On pyrolysis, ureas (2) are converted into the meso-ionic compound 5,7-diphenyl-1,3,4-oxadiazolo[3,2-a] pyridinium--2-olate (3, X=0) (m.p.201°; 82%) and the respective amine. The reaction can be performed by simple heating of urea (2) at 250° for 30 minutes. Meso-ionic compound (3, X=0) has also been prepared from (1) by reaction with NN'-carbonyldiimidazole (37%). Support for the formulation (3) is clearly provided by its i.r. spectrum. The compound (3, X=0) shows a strong band in the carbonyl region (1770 cm<sup>-1</sup>) which may be compared in position with the carbonyl band shown by isosydnones (1758-1770 cm<sup>-1</sup>)<sup>3</sup> and derivatives of the 1,3,4-oxadiazolo[3,2-a] pyridinium-2-olate (1775 cm<sup>-1</sup>) reported by Hoegerle<sup>2</sup>.

b) Via iminophosphorane (4).

1-Triphenylphosphinoimino-4,6-diphenyl-2-pyridone (4), readily available from (1) by reaction with triphenylphosphine dibromide, reacts with carbon disulphide to yield the meso-ionic compound 5,7-diphenyl-1,3,4-oxadiazolo[3,2-a] pyridinium-2-thiolate (3, X=S) (m.p.216°; 76%). Its i.r. spectrum shows an absorption in the 1430 cm<sup>-1</sup> region which can be attributed to thione stretching<sup>4</sup>. Only one derivative of this ring system has been previously described<sup>5</sup>. Similarly, the iminophosphorane (4) reacts with arylisocyanates or isothiocyanates to give the respectives 5,7-diphenyl-1,3,4-oxadiazolo[3,2-a] pyridinium-2-aminides (5, Ar=C<sub>6</sub>H<sub>5</sub>) (m.p.208°; 81%) and (5, Ar=  $\alpha$ -C<sub>10</sub>H<sub>7</sub>) (m.p.236°; 86%). These compounds have also been prepared by an alternative route that involves the action of the reagent triphenylphosphine/carbon tetrachloride on uneas (2). The i.r. spectra of (5) show a strong absorption at 1630 cm<sup>-1</sup> which can be attributed to exocyclic C=N stretching<sup>6</sup>.

Dipole moments of  $(\underline{3}, X=0)$  (7.85 D),  $(\underline{3}, X=S)$  (9.15 D) and  $(\underline{5}, Ar=C_6H_5)$  (7.61 D) in benzene solution have been measured and are in excellent agreement with the meso-ionic structures indicated. The analytical data and mass spectra support this assumption.



## References

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(Received in UK 6 August 1980)