

## Condensed Heterocycles — Morgan-Walls Cyclization of N-(2-Diphenyl)pyrrolidone\*†

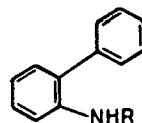
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**Cyclization of N-(2-biphenyl)-2-pyrrolidone(IV) with  $\text{POCl}_3$  affords the dimeric phenanthridinium derivative VIII instead of the expected tetracyclic derivative V. A mechanism of formation of VIII is suggested.**

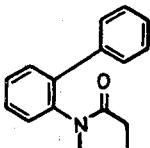
**CYCLIZATION** of *o*-xenylamides (II) by  $\text{POCl}_3$  constitutes the basis for the well-known Morgan-Walls synthesis of phenanthridines<sup>1</sup>. We wished to prepare the quaternary compound (V) under the same conditions from the pyrrolidone (IV). Treatment of 2-aminodiphenyl (I) with  $\gamma$ -bromobutyryl chloride gave amide (III), which was converted by sodium hydride in refluxing dioxane into the pyrrolidone (IV). The latter was heated with an excess of  $\text{POCl}_3$  under reflux. The product could not be characterized as chloride or iodide; but a crystalline perchlorate, m.p. 178-80° was obtained, which had the characteristic UV spectrum of phenanthridine. Elementary analysis revealed at once that it was not the perchloric acid salt of V. But the values were in agreement with those calculated for the dimeric structure VII. This was confirmed further as follows: passage of VII through Amberlite IRA-400 (Cl<sup>-</sup> form) gave the



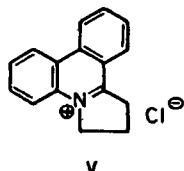
I : R = H

II : R = COR<sub>1</sub>

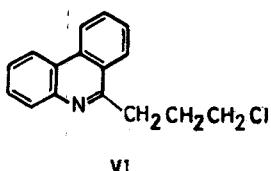
III : R = COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br



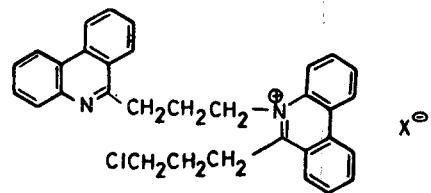
IV



V



VI



VII X = ClO<sub>4</sub>

VIII X = Cl

amorphous chloride (VIII) which showed the presence of approximately two chlorine atoms per molecule (Found: 12.60; calculated 13.86%), of which one was ionic (Found: 7.62; calc. 6.93%). We like to speculate that IV initially cyclizes to V, which can suffer nucleophilic attack on carbon by chlorine to form VI. Follow-up by nucleophilic attack by nitrogen atom in VI on the carbon atom bearing the quaternary nitrogen atom in V or on the carbon atom bearing chlorine in another molecule of its own kind would result in the formation of VIII.

**N-( $\gamma$ -Bromobutyryl)-2-aminodiphenyl (III)**—To a stirred and ice-water cooled mixture of 2-aminodiphenyl (I) (5.1 g) in ether (100 ml) and  $\text{NaHCO}_3$  (2.6 g) in water (50 ml), was added  $\gamma$ -bromobutyryl chloride (5.6 g) in ether (25 ml). After being stirred overnight at room temperature, the mixture was filtered and the precipitated amide (III) washed with water, dil. HCl and again with water; yield 8.4 g, m.p. 78-80°. A sample was crystallized from hexane; m.p. 80-82° (Found: C, 60.23; H, 5.39; N, 4.38.  $\text{C}_{16}\text{H}_{16}\text{BrNO}$  requires, C, 60.39; H, 5.07; N, 4.40%); IR (nujol) 3260 (NH), 1650 (C=O)  $\text{cm}^{-1}$ .

**N-(2-Diphenyl)-2-pyrrolidone (IV)**—A solution of amide (III, 15 g) in dry dioxane (200 ml) containing 50% sodium hydride suspension in mineral oil (2.7 g) was heated under reflux for 6 hr. The mixture was filtered and the filtrate freed from dioxane *in vacuo*. The residual oil (~14 g) was chromatographed over a column of silica gel (150 g; E. Merck, 0.05-0.2 mm) in benzene-chloroform (1:3). The column was developed with the same solvent, and 50 ml fractions were taken from the eluate. Earlier fractions containing III were discarded. Fractions 13-25 which were reasonably homogeneous (TLC) were combined and evaporated to give IV as an oil (7 g) which was further purified by bulb to bulb distillation at 150-60° (bath)/0.1-0.2 mm (Found: C, 80.81; H, 6.57; N, 6.19.  $\text{C}_{16}\text{H}_{15}\text{NO}$  requires C, 80.98; H, 6.37; N, 5.9%);  $\nu_{\text{max}}$  1700 (C=O)  $\text{cm}^{-1}$ .

**$\text{POCl}_3$  cyclization of lactam (IV)**—A mixture of lactam (IV, 2 g) and  $\text{POCl}_3$  (30 ml) was heated under reflux for 6 hr. Excess  $\text{POCl}_3$  was removed *in vacuo*; the residual oil was washed with ice water and ether, then dissolved in 10 ml ethanol and treated with 70%  $\text{HClO}_4$  (2 ml). The crystalline perchlorate (VII) separated and was filtered off and recrystallized from ethanol; 2 g, m.p. 180-81° (Found: C, 66.80, 66.99; H, 5.32, 5.37; N, 5.22, 5.28; Cl, 11.85, 12.32.  $\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{N}_2\text{O}_4$  requires C, 66.67; H, 5.07; N, 4.86; Cl, 12.30%).  $\lambda_{\text{max}}^{\text{EtOH}}$  236, 375, 462 (infl.), 483 nm (log  $\epsilon$  4.43, 4.49, 3.34, 3.43); NMR (in  $\text{DMSO}-d_6$ ; chemical shifts downfield from TMS internal standard):  $\delta$  2.1 (broad s, 4H); 3.6 (very broad s, 8H), 7.5 (broad s, 12 aromatic protons). A methanolic solution of V did not give a precipitate with  $\text{AgNO}_3$  in dil. nitric acid, but brief treatment of V with 10% NaOH liberated chloride ion.

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### References

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\*Contribution No. 285 from CIBA Research Centre.

†For the earlier paper in this series, see Nagarajan, K., Ranga Rao, V. & Venkateswarlu, A., *Indian J. Chem.*, 10 (1972), 344.

