A MILD AUTOXIDATION OF 3,4-DIPHENYL-2-FURYL CARBAMATES TO 3,4-DIPHENYL-5-HYDROXY-3-PYRROLIN-2-ONES

Kazuo Ito* and Kenichi Yakushiji
Faculty of Pharmacy, Meijo University, Nagoya, Japan

3,4-Diphenyl-2-furyl carbamates (Ia-c) react with oxygen in benzene at room temperature to give 3,4-diphenyl-5-hydroxy-3-pyrrolin-2-ones (IIa-c) as the sole product.

We recently reported that the thermal cyclization of 3,4-diphenyl-2-furyl isocyanate gave 1-phenylfuro[2,3-c]isoquinolin-5(4H)-one in good yield\(^1\). In connection with this work, 3,4-diphenyl-2-furyl carbamates (Ia-c) were synthesized\(^2\). This communication deals with the novel ring transformation of 2-aminofuran I to pyrrolinones II by a mild autoxidation\(^3\).

3,4-Diphenyl-2-furyl carbamates (Ia-c) were prepared in good yields by refluxing of 3,4-diphenyl-2-furoyl azide\(^1\) with corresponding alcohols in benzene. A solution of Ia (2 mmoles) in benzene (20 ml) was stirred with oxygen in diffuse daylight. After about 2 hr, colorless crystals began to precipitate. The product which was filtered after 24 hr stirring afforded N-carbobenzyloxy-3,4-diphenyl-5-hydroxy-3-pyrrolin-2-one (IIa, R=CH\(_2\)Ph), mp 170-171\(^\circ\), in 64\% yield. The structure of IIa was confirmed on the basis of spectral data; NMR (CDCl\(_3\)) \(\delta\) 7.24 (15H, m, Ph x 3),
6.31 (1H, d, J=5 Hz, collapsing with D₂O to singlet), 5.31 (2H, s, CH₂), 4.15 (1H, d, OH, J=5 Hz, vanishing with D₂O); IR (KBr) cm⁻¹ 3440 (OH), 1732 and 1688 (CO). The following chemical properties also supported the structure \( \ce{\text{a}} \). Treatment of \( \ce{\text{a}} \) with Ac₂O in pyridine at room temperature gave N-carbobenzyloxy-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (\( \ce{\text{b}} \), mp 168-169°; NMR (CDCl₃) δ 7.72 (1H, s, C₅-H), 7.29 (15H, m, Ph x 3), 5.43 and 5.18 (2H, d x 2, CH₂, J=12 Hz), 1.80 (3H, s, CH₃); IR (KBr) cm⁻¹ 1755, 1739 and 1722 (CO).

Also, hydrogenolysis of \( \ce{\text{a}} \) with hydrogen over Pd/C in ethanol gave 3,4-diphenyl-3-pyrrolin-2-one (\( \ce{\text{c}} \), mp 192-193°; NMR (CDCl₃) δ 7.40 (11H, m, Ph x 2 and NH), 4.43 (2H, s, C₅-H); IR (KBr) cm⁻¹ 3170 and 1670 (NHCO). Similar autoxidation of \( \ce{\text{b}} \) and \( \ce{\text{c}} \) in benzene gave the corresponding pyrrolinones \( \ce{\text{d}} \) (62%) and \( \ce{\text{e}} \) (43%), and these compounds were acetylated to give \( \ce{\text{f}} \) and \( \ce{\text{g}} \), respectively.

The formation of pyrrole by autoxidation of 2-aminofuran has been described in literatures. We propose the following mechanism for the reaction (see Scheme). Addition of molecular oxygen to \( \ce{\text{i}} \) gives dioxetanes \( \ce{\text{A}} \). The cleavage of \( \ce{\text{A}} \) with loss of oxygen atom forms γ-ketoamides \( \ce{\text{h}} \) which is spontaneously cyclized to \( \ce{\text{a}} \). In
autoxidation of $\lambda$ described above, diphenylacetylene, diphenylmaleic anhydrides and 9,10-phenanthrenedicarboxylic anhydrides were also confirmed as by-products\textsuperscript{5).}

References and Notes

5) We will report elsewhere.

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