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

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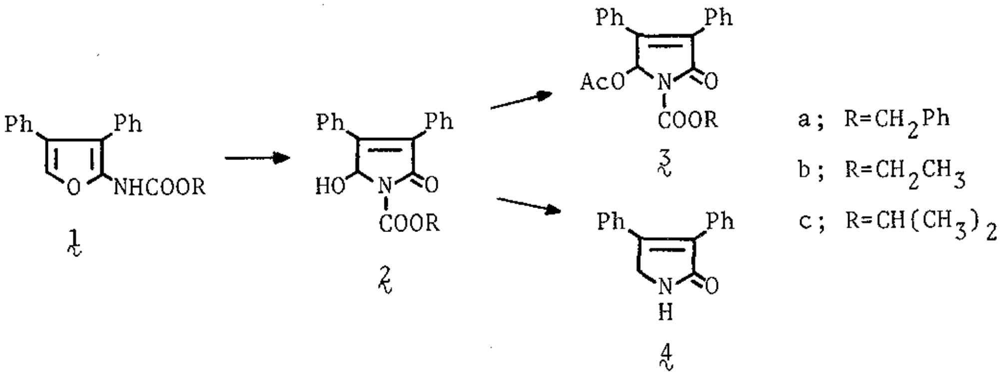
3,4-Diphenyl-2-furyl carbamates (**1a**-**c**) react with oxygen in benzene at room temperature to give 3,4-diphenyl-5-hydroxy-3-pyrrolin-2-ones (**2a**-**c**) as the sole product.

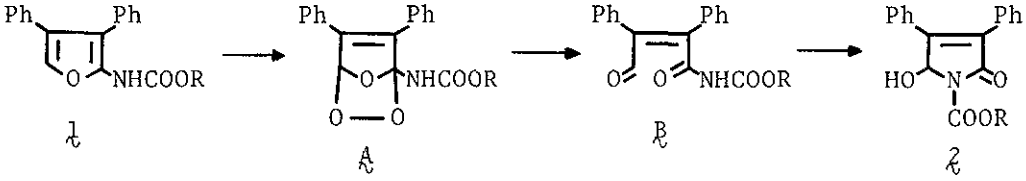
We recently reported that the thermal cyclization of 3,4-diphenyl-2-furyl isocyanate gave 1-phenylfuro[2,3-c]isoquinolin-5(4H)-one in good yield$^{1)}$. In connection with this work, 3,4-diphenyl-2-furyl carbamates (**1a**-**c**) were synthesized$^{2)}$. This communication deals with the novel ring transformation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

3,4-Diphenyl-2-furyl carbamates (**1a**-**c**) were prepared in good yields by refluxing of 3,4-diphenyl-2-furoyl azide$^{1)}$ with corresponding alcohols in benzene. A solution of **1a** (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 (**2a**, R=CH_2Ph), mp 170-171°, in 64% yield. The structure of **2a** was confirmed on the basis of spectral data; NMR ($CDCl_3$) δ 7.24 (15H, m, Ph x 3),



6.31 (1H, d, J=5 Hz, collapsing with D_2O to singlet), 5.31 (2H, s, CH_2), 4.15 (1H, d, OH, J=5 Hz, vanishing with D_2O); IR (KBr) cm^{-1} 3440 (OH), 1732 and 1688 (CO). The following chemical properties also supported the structure **2**. Treatment of **2a** with Ac_2O in pyridine at room temperature gave N-carbobenzyloxy-5-acetoxy-3,4-diphenyl-3-pyrrolin-2-one (**3a**, R=CH_2Ph), mp 168-169°; NMR ($CDCl_3$) δ 7.72 (1H, s, C_5-H), 7.29 (15H, m, Ph x 3), 5.43 and 5.18 (2H, d x 2, CH_2, J=12 Hz), 1.80 (3H, s, CH_3); IR (KBr) cm^{-1} 1755, 1739 and 1722 (CO). Also, hydrogenolysis of **2a** with hydrogen over Pd/C in ethanol gave 3,4-diphenyl-3-pyrrolin-2-one (**4**), mp 192-193°; NMR ($CDCl_3$) δ 7.40 (11H, m, Ph x 2 and NH), 4.43 (2H, s, C_5-H); IR (KBr) cm^{-1} 3170 and 1670 (NHCO). Similar autoxidation of **1b** and **1c** in benzene gave the corresponding pyrrolinones **2b** (62%) and **2c** (43%), and these compounds were acetylated to give **3b** and **3c**, 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 **1** gives dioxetanes **A**. The cleavage of **A** with loss of oxygen atom forms γ-ketoamides **B**[4] which is spontaneously cyclized to **2**. In



Scheme

autoxidation of 1 described above, diphenylacetylene, diphenylmaleic anhydrides and 9,10-phenanthrenedicarboxylic anhydrides were also confirmed as by-products[5].

References and Notes

1) K. Ito, K. Yakushijin, S. Yoshina, A. Tanaka and K. Yamamoto, J. Heterocyclic Chem., 1978, 15, 301.

2) Winters, et al. described that the thermal cyclization of β-phenyl-α-carbamoyl heterocyclic compounds produced fused isoquinolinones; G. Winters and N. Di Mola, Tetrahedron Lett., 1975, 3877.

3) Autoxidation of organic substrates with oxygen at room temperature in the absence of catalysts or bases has been known on a relatively small group, including certain hydrocarbons[a], enamines[b], hydrazones[c], enols[d] and phenols[e]; a) W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang and P. v. R. Schleyer, J. Amer. Chem. Soc., 1974, 96, 4301. b) J. Rigaudy, J. Barcelo and C. Igier, Bull. Soc. chim. France, 1974, 1151. c) E. G. E. Hawkins, J. Chem. Soc. (C), 1971, 1474. d) P. R. Enslin, Tetrahedron, 1971, 27, 1909; R. Stevens and D. Wright, J. Chem. Soc., 1963, 1763. e) J. Carnduff and D. G. Leppard, J. Chem. Soc. Perkin I, 1976, 2570; B. Miller, Chem. Comm., 1971, 574.

4) Boyd, et al. described the formation of pyrrolinones from γ-ketoamides; G. V. Boyd and K. Heatherington, J. Chem. Soc. Perkin I, 1973, 2523.

5) We will report elsewhere.

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