

Dimerization of Pyrroles by Palladium Acetate. New Synthesis of 2,2'-Bipyrroles

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Summary Oxidation of 1-arylpyrroles by palladium acetate in acetic acid gave the corresponding 1,1'-diaryl-2,2'-bipyrroles, which were easily hydrolysed in MeOH-H₂O containing HCl to give 2,2'-bipyrrole

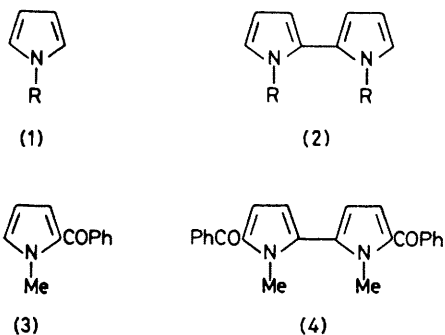
IN recent years increasing interest has been shown in the chemistry of polypyrroles. 2,2'-Bipyrroles (**2**) are of interest owing to their connection with naturally occurring compounds such as prodigiosins¹ and vitamin B₁₂. However, no easy and simple method for the preparation of (**2**) has been found, although Rapoport and Castagnoli² have reported the synthesis of 2,2'-bipyrrole (**2a**) from 2-pyrrolidin-2-ylpyrrole. Little attention has been paid to the dimerization of pyrroles as an efficient method for the preparation of (**2**) although coupling reactions of olefins or aromatic com-

pounds are well known. We now find that oxidation of 1-aroilpyrroles (**1b—d**)³ by palladium acetate in acetic acid gives the corresponding 1,1'-diaroil-2,2'-bipyrroles (**2b—d**) in good yields. 2,2'-Bipyrrole (**2a**) is obtained by hydrolysis of (**2b—d**) in high yield and this reaction provides an efficient and simple method for its synthesis.

A solution of 1-benzoylpyrrole (**1b**) and 0.34 equiv. of palladium acetate in acetic acid was heated at 110 °C under nitrogen for 10 h. The mixture was evaporated to give a dark orange oily residue which was chromatographed on silica gel to give (**2b**),[†] m.p. 150—151 °C, in 47% yield (conv.[‡] 64%). Under similar conditions 1-*p*-methylbenzoylpyrrole (**1c**) and 1- α -naphthoylpyrrole (**1d**) reacted to give (**2c**), m.p. 190—192 °C (yield 43%, conv. 78%), and (**2d**), m.p. 225—227 °C (yield 56%, conv. 76%), respectively. Attempted dimerization of 1-methyl- and 1-acetylpyrroles failed under similar conditions, however. In an effort to determine the effect of the aroil group on the dimerization of pyrroles, the oxidation of 2-benzoyl-1-methylpyrrole (**3**) by palladium acetate was investigated. The expected compound (**4**), m.p. 185—187 °C, was obtained in 38% yield (conv. 89%).

Treatment of (**2b**) in MeOH-H₂O with HCl at 60 °C for 6 h gave (**2a**), m.p. 189—190 °C (lit.² 189—190 °C) in 93% yield. Under similar conditions hydrolysis of (**2c**) and (**2d**) also gave (**2a**).

(Received, 15th October 1979, Com. 1092.)



- a**; R = H
b; R = PhCO
c; R = *p*-MeC₆H₄CO
d; R = α -Naphthoyl

[†] New compounds were fully characterized spectroscopically (n.m.r., i.r., and mass) and by elemental analysis.

[‡] Percentage yield taking into account recovered starting material.

¹ H. H. Wasserman, J. E. McKeon, L. Smith, and P. Forgione, *J. Amer. Chem. Soc.*, 1960, **82**, 506; H. Rapoport and K. G. Holden, *ibid.*, 1962, **84**, 635.

² H. Rapoport and N. Castagnoli, *J. Amer. Chem. Soc.*, 1962, **84**, 2178.

³ The preparation of 1-aroilpyrroles from pyrrole was carried out by applying the method used for the synthesis of 1-aroilindoles (T. Itahara, *Synthesis*, 1979, 151).