

THE PYROLYSIS OF SOME ANHYDRIDES OF THE PYRROLE SERIES

M. P. Cava¹ and L. Bravo

Department of Chemistry, Wayne State University,

Detroit, Michigan 48202

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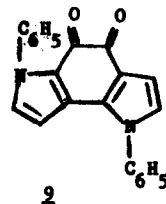
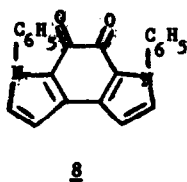
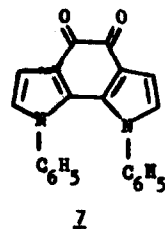
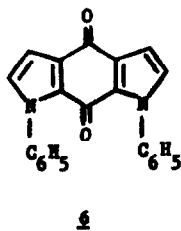
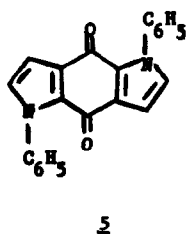
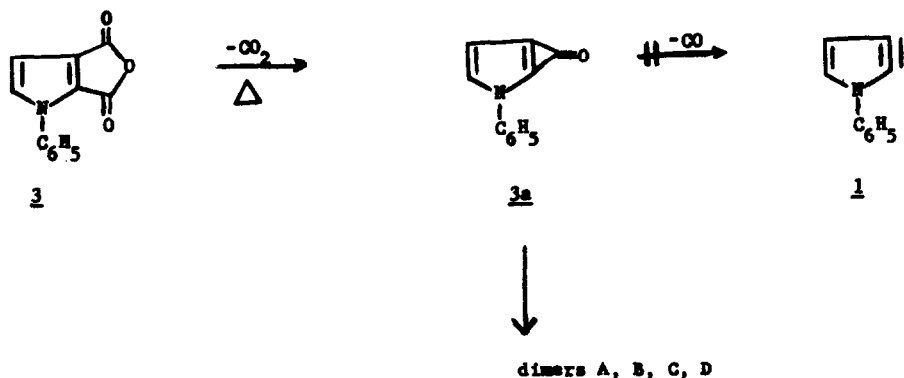
Department of Chemistry, University of Pennsylvania,

Philadelphia, Pennsylvania 19104

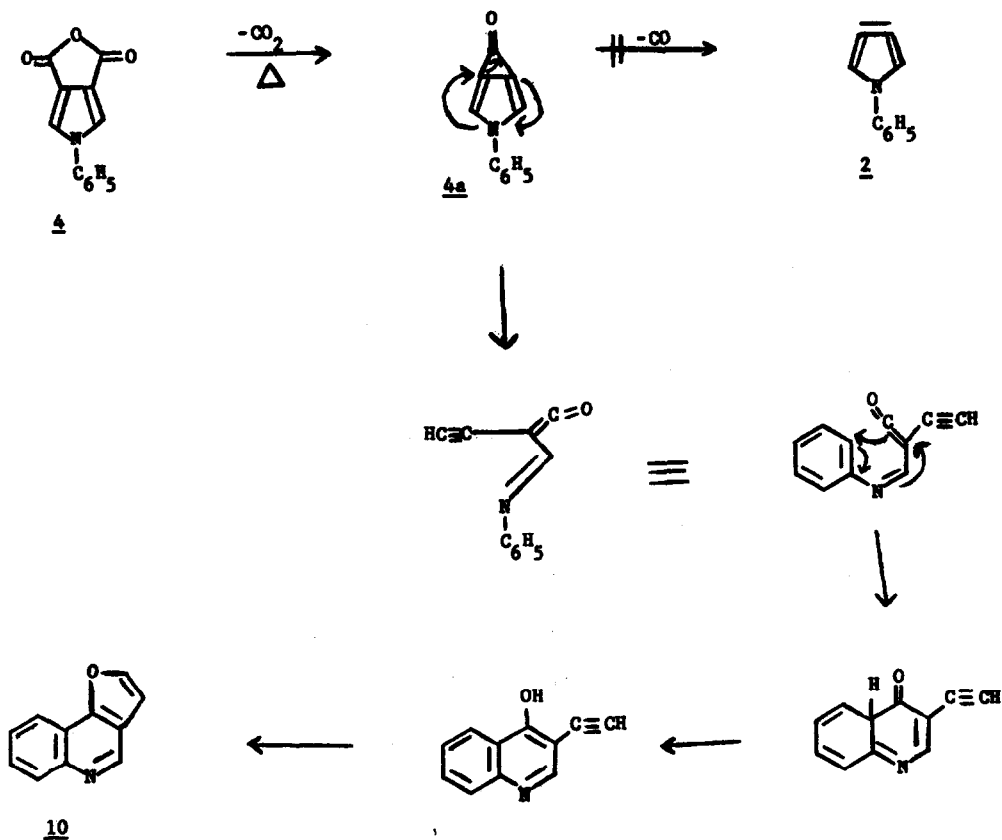
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Heteroarynes have been generated by the gas phase pyrolysis of a variety of dicarboxylic anhydrides of six-membered nitrogen-containing heterocycles; in all cases reported the heteroaryne initially produced undergoes subsequent ring cleavage followed by rearrangement.² No unambiguous evidence has yet been presented for the formation by any method of a heteroaryne derived from a five-membered aromatic heterocycle.³ For this reason, we decided to attempt the generation of 1-phenyl-2,3-dehydropyrrole (1) and 1-phenyl-3,4-dehydropyrrole (2) by the pyrolysis of the appropriate anhydride precursors 3 and 4.

Pyrolysis of 1-phenylpyrrole-2,3-dicarboxylic anhydride (3)⁴ was carried out in a stream of dry nitrogen (12 mm pressure) over a glowing Nichrome coil. The pyrolysate afforded, in 60% yield (based on unrecovered 3), a mixture of four colored compounds A, B, C and D, which were separated with difficulty chromatographically. All of these compounds had molecular weights of 338, corresponding to the loss of carbon dioxide from anhydride 3, followed by dimerization; all showed a strong carbonyl band in the infrared in the 6 μ region. In addition, the nmr spectrum of A (yellow, m.p. 291-292^o) showed only a singlet at δ 7.5 (10 H) and an AB quartet (4 H) at δ 6.88 and δ 6.66 (J = 2.9 Hz). The nmr spectrum of B (orange, m.p. 246-247^o) was very similar showing a singlet at δ 7.4 (10 H) and an AB quartet at δ 6.87 and δ 6.78 (4 H, J = 2.9 Hz). Compounds A and B were assigned the anthraquinone-like structures 5 and 6 (or vice-versa), an assignment which was supported by the formation of A and B in low yield (but not C or D) from the reaction of anhydride 3 with 1-phenylpyrrole in polyphosphoric acid. Compounds C (sepia, m.p. 239-243^o) and D (pink, m.p. 315^o) were incompletely characterized due to paucity of material; the phenanthrenequinone-like structures 7, 8 or 9 are tentatively suggested for them.



Pyrolysis of 1-phenylpyrrole-3,4-dicarboxylic anhydride (**4**)⁵ was carried out as with anhydride **3**. The sole product obtained, in 81% yield (based on unrecovered **4**), had a molecular weight of 169 (4-CO_2) and formed colorless needles, m.p. 35-36°. This product was found to be identical with the known furo[3,2-c]quinoline (**10**) by direct comparison (ir, uv, nmr, mp) with authentic material.⁶ A rational mechanism for this complex, but remarkably clean, rearrangement is proposed below.



Although the mass spectra of anhydrides **3** and **4** show peaks corresponding to the dehydropyrroles **1** and **2** (of relative intensities 79% and 15%, respectively), it is clear that at the rather high pyrolysis temperature employed (650°), the intermediate cyclopropenones **3a** and **4a** (or the corresponding open diradicals) do not tend to lose carbon monoxide to give dehydropyrroles but are instead diverted to other products by dimerization or rearrangement.

Anhydrides **3** and **4** are the first reported examples of aromatic anhydrides which do not give pyrolysis products derived from aryne intermediates.⁷ This behavior is in good agreement with the reluctance of other types of reactions to give five-membered heteroaryne intermediates, structures in which very poor orbital overlap must exist in the formal triple bond.

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REFERENCES

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