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THE STRUCTURE OF 2,3,5-TRISUBSTITUTED 2-PYRROLIN-4-ONES

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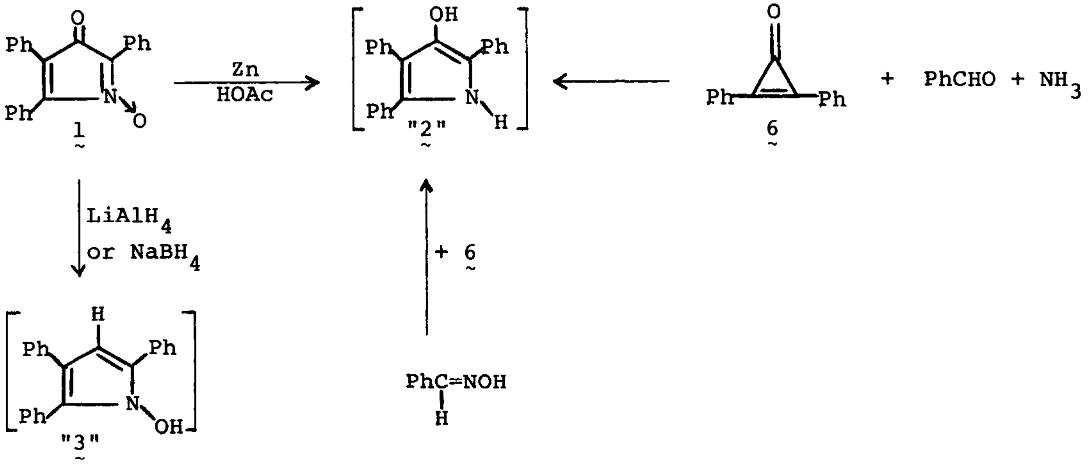
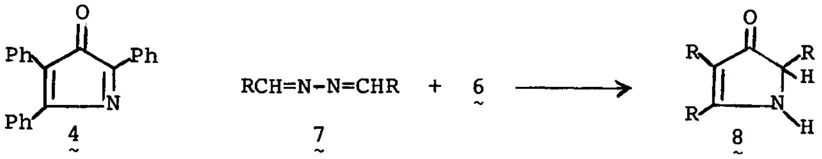
Abstract: Compounds previously reported to be 2,3,5-trisubstituted 2-pyrrolin-4-ones are shown to have 5,5'-dimeric structures.

Recently, the reduction of 2,4,5-triphenyl-3H-pyrrol-3-one 1-oxide (1) with Zn-HOAc was reported[1] to give 3-hydroxy-2,4,5-triphenylpyrrole "2", (73%), whereas the reduction of 1 with either $LiAlH_4$ or $NaBH_4$ was said to yield 1-hydroxy-2,4,5-triphenylpyrrole[2] "3", (78% and 62% respectively). The mass spectra of "2" and "3" were found to have almost "identical fragmentation pathways".[3]

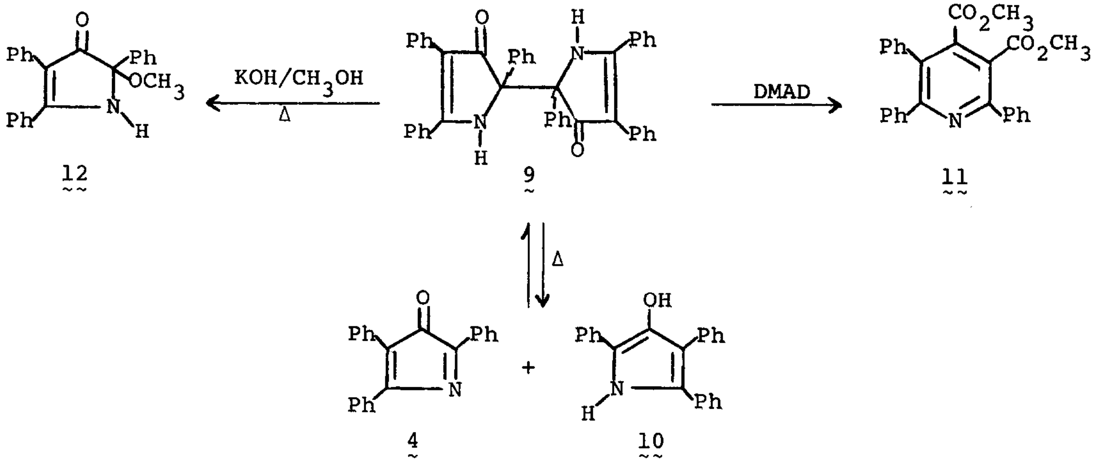
In connection with another project we sought a synthesis of 2,4,5-triphenyl-3H-pyrrol-3-one 4, and envisaged the oxidation of "2" as a possible route to 4. On repeating the reported[1] preparation of "2", we were surprised at the insolubility of "2" in the usual organic solvents, and at the presence of a strong band at 1640 cm^{-1} in its infrared spectrum in addition to a band at 3200 cm^{-1}. The former IR band is inconsistent with the assigned structure of "2".





In analogy to the work of Eicher and coworkers,[4] we found that a methanolic solution of benzaldehyde and excess ammonia reacted immediately with diphenylcyclopropenone 6 and gave "2" in 80% yield. Furthermore, benzaldehyde oxime reacted with 6 in refluxing toluene and yielded "2" (31%), and traces of 4. Recently, Takahashi and coworkers[5] reported the preparation of a number of "2,3,5-trisubstituted 2-pyrrolin-4-ones 8" by the reaction of azines 7 with 6. We found that product 8 (R = Ph) was identical to "2".[6]

We propose that product "2" is a dimer of the alleged 3-hydroxy-2,4,5-triphenylpyrrole "2" or its tautomer 8 (R = Ph). The mass spectrum of 9 (inlet temperature 330°C) showed two peaks at 311 and 309 consistent with structures 10 and 4 respectively. A chemical ionization (CH_4) mass spectrum of 9 showed a peak at 442 (M^+ -178 (PhCCPh), 22%). The infrared spectrum of 9 showed strong bands at 3220 and 1640 cm^{-1} while the nmr spectrum ($CDCl_3$) did not show any signal from 2-6 δ.



Heating a slurry of 9 in triglyme gives a deep violet-red color which fades upon cooling. The color is presumed to be due to pyrrolone 4. Dimer 9 reacted smoothly with dimethylacetylenedicarboxylate (DMAD) at reflux temperature and gave pyridine 11[1,7] in 52% yield. The reaction of 9 with 5% methanolic KOH (reflux, 5 hr.) gave 12 (50%); m/e: M^+ 341, 309 (M^+-CH_3OH), ir: 3230, 1670 cm^{-1}; nmr: δ 3.5 (3 H), 7.8-7.2 (m, 15 H). Product 12 was identical to that obtained from the addition of methanol to a CH_2Cl_2 solution of 4.[8]

In our hands the reduction of 1 with $NaBH_4$ gave 9 as the major product, while the reduction with $LiAlH_4$ gave a pale yellow solid 10 which was soluble in the usual organic solvents; ir: 3480-3200, 1600 cm^{-1}; nmr: δ 3.5 (br.s., 1 H), 7.8-7.1 (m, 15 H), 8.5 (br., 1 H). Addition of 10 to 4 in CH_2Cl_2 resulted in the instantaneous discharge of the violet color of 4 and the subsequent precipitation of 9. Since 10 was converted to 9, immediately in the air in alcoholic base and upon standing for a week in $CHCl_3$, it appears to have the monomeric structure previously attributed to 2 and 8. Crude 10 melted at 60-65°C and started to dimerize above 120°C.

The dimerization of 10 into 9 either by air oxidation or by the addition to 4 has a number of analogies in the literature especially in the chemistry of indoxyls[9a,b,c,d] and 3-furanones.[10] The Zn-HOAc reduction of 2-phenylisatogen to a dimer is closely analogous to the reduction of 1.[9b]

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6. We thank Dr. Takahashi for a sample of **8** (R = Ph).

7. T. Eicher, F. Abdesaken, G. Franke, and J. L. Weber, *Tetrahedron Lett.*, *1975*, 3915. Pyridine **11** reported in this paper is identical to that reported in ref. **1**; the correct mp is 231°C as reported in ref. **1**.

8. The generation of **4** in solution will be described in a separate publication.

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