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ON THE PHOTO-OXIDATION OF 3,4-DIETHYL-2-METHYLPYRROLE*

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Although the photo-oxidation of pyrrole[1] and various phenyl substituted pyrroles[2-5] has been studied extensively, such has not been the case with alkylpyrroles and the nature of their photo-oxidation products is largely unknown. Alkylpyrroles are unstable in the presence of air and light,[6,7] but only the autooxidation products of 2,4-dimethylpyrrole, 2,3,4-trimethylpyrrole and 2,4-dimethyl-3-ethylpyrrole have had their structures proved.[7] In this communication we report on the first photo-oxygenation of a trialkylpyrrole in which we have discovered several new types of products one of which involves dealkylation of an α-alkyl substituent.

3,4-Diethyl-2-methylpyrrole[8] (1), was photolyzed[9] as a dilute (0.2% w/v) methanolic solution containing 3 mg % Rose Bengal ($^1O_2$ sensitizer) for four hours while bubbling a slow stream of oxygen through the reaction vessel. After evaporation of the methanol *in vacuo* at room temperature, the crude photolysate was chromatographed on a silica gel column (E. Merck, Darmstadt). Ethyl acetate eluted three components (60% of the total photolysate) which were separated by preparative thin-layer chromatography on silica gel (M. Woelm, Eschwege, 1 mm, ether).

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[*] Pyrrole Photo-oxidation II. For the preceding paper see G. B. Quistad and D. A. Lightner, *Chem. Commun.*, 1099 (1971).

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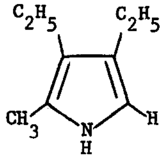

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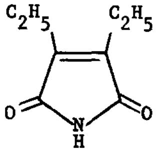

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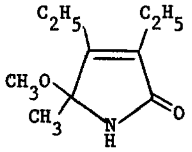

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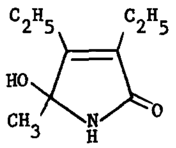

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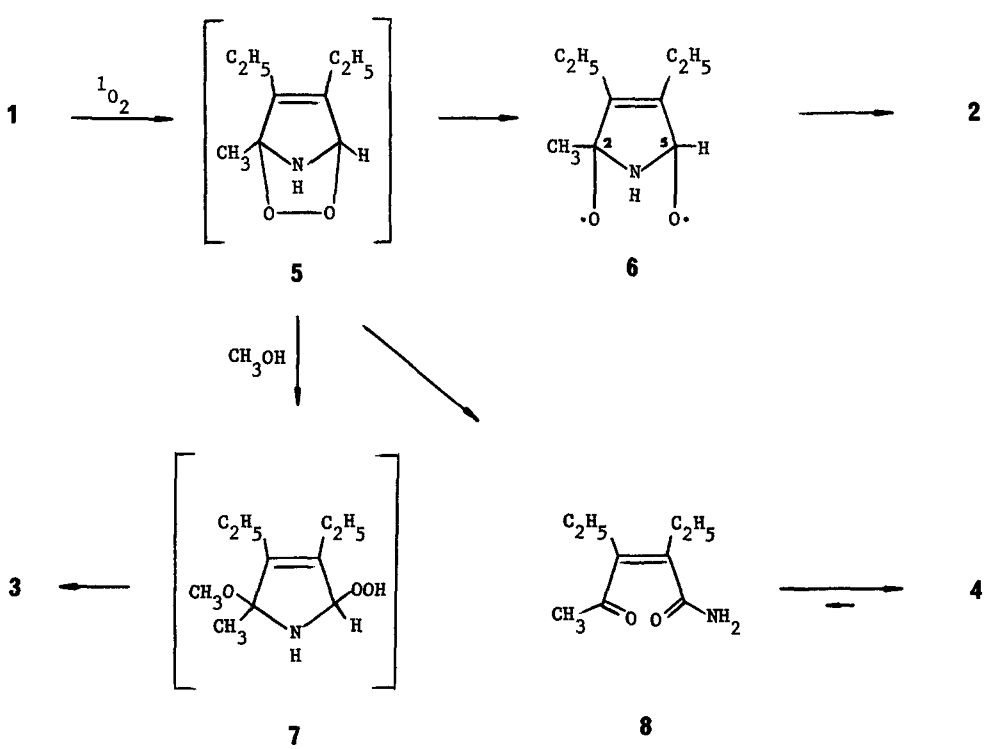
A product of R_f 0.93 was obtained in 3% yield and proved to be diethylmaleimide (2) [mp 66-69°, (lit. mp 68°)[10]] which was characterized by comparison with an authentic sample. A second product, yellow oil (11%), R_f 0.47, was identified as 3,4-diethyl-5-methoxy-5-methyl-3-pyrrolin-2-one (3). The structure of 3 was confirmed by its nuclear magnetic resonance spectrum (nmr):[11] (CCl_4) δ 1.03 (t, 3H, CH_3, J = 8 Hz), 1.12 (t, 3H, CH_3, J = 8 Hz), 1.43 (s, 3H, CH_3), 2.22 (q, 4H, 2 CH_2, J = 8 Hz), 2.91 (s, 3H, OCH_3), 7.72 (s, 1H, N-H); and its mass spectrum:[11] m/e (relative intensity) 183 [M^+] (18%), 168 [$M-CH_3$] (22%), 152 [$M-OCH_3$] (100%). The major product, R_f 0.25, (40%) proved to be 3,4-diethyl-5-hydroxy-5-methyl-3-pyrrolin-2-one (4), mp 121-123° after recrystallization from carbon tetrachloride-hexane. The structure of 4 was established from its nmr spectrum: (CCl_4) δ 0.99 (t, 3H, CH_3, J = 8 Hz), 1.16 (t, 3H, CH_3, J = 8 Hz), 1.46 (s, 3H, CH_3), 2.10 (q, 2H, CH_2, J = 8 Hz), 2.31 (q, 2H, CH_2, J = 8 Hz), 7.73 (s, 1H, N-H): its mass spectrum m/e (relative intensity) 169 [M^+] (43%), 154 [$M-CH_3$] (59%), 151 [$M-H_2O$] (53%), 140 (99%), 136 (100%); and its infrared spectrum:[11] ($CHCl_3$) 3330 cm^{-1} (O-H), 1685 (C=O).

In the preceding results, we observed the first dealkylation of an alkylpyrrole resulting in direct formation of an imide photoproduct (2).[12] The dealkylation reaction probably proceeds via the presumed intermediate endoperoxide (5)[1,12] as shown in Scheme 1 first by thermal homolysis of the O-O bond (to 6) followed by loss of a methyl radical [cf t-butoxy radical → acetone + methyl radical[13]] and a hydrogen atom. The formation of 5-methoxylactam (3) was expected from photolysis of 1 in methanol. Similar products are found from the dye-sensitized photo-oxidation of furan,[14] pyrrole[1,12] and 3,4-diethylpyrrole.[12] However, 2-methylfuran and 2,5-dimethylfuran give the 2-methyl-5-hydroperoxy product.[14,15] A probable mechanism for the formation of 3 involves attack by methanol at C-2 to open the endoperoxide ring (Scheme 1). The resultant hydroperoxide (7) is not isolated and presumably rapidly decomposes to 3. The predominant formation of the 5-hydroxylactam (4)

Scheme 1



was unanticipated and an equivalent reaction has not been reported previously in other pyrrole photo-oxidations. Whether the mechanism involves an intramolecular source of hydrogen (*viz.* the N-H or C_5-H) or H-abstraction occurs from methanol is not clear. An intermediate such as 6 could presumably collapse directly to 4 simply by transfer of the C_5-H to the oxygen at C-2. However, an alternative mechanism (Scheme 1) might involve collapse of 5 to the α,β-unsaturated keto-amide 8 followed by cyclization to 4. The mechanistic details of these reactions and studies on the photo-oxidation of other alkylated pyrroles are currently under investigation in our laboratories.

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9. Colortran tungsten-halogen quartz lamp, Berkey-Colortran Inc., 120 volt, 1000 watt, code B-5-32, run at 50 volts.
10. Reference 7, p. 398.
11. All mass spectra were determined on a CEC 491 MS-21; all nuclear magnetic resonance spectra were run on a Varian T-60 instrument; infrared spectra were recorded using a Perkin-Elmer 700 spectrometer.
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