Pyrrole Photo-oxidation. Unusual Products from 2,5-Dimethylpyrrole[1]

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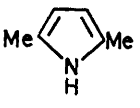
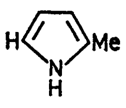
Summary The dye-sensitised photo-oxygenation of 2,5-dimethylpyrrole in methanol yields the dealkylation products 5-methoxy-5-methyl-Δ^3-pyrrolin-2-one and 5-methoxy-5-methoxymethyl-Δ^3-pyrrolin-2-one in addition to the surprising structure, 2-formyl-2-methoxy-5-methylidene-Δ^3-pyrroline; similar photo-oxidation of 2-methylpyrrole gives 5-methoxy-5-methyl-Δ^3-pyrrolin-2-one as the major product.

DESPITE the early observation that alkylpyrroles were susceptible of auto-oxidation[2] and later reports on the proof of structure of the products,[3] their photo-oxidation reaction has been studied only recently.[1,4] Other work on the photo-oxygenation of pyrrole compounds has been devoted largely to a study of pyrrole itself[5] and various phenyl substituted pyrroles.[6] We describe the dye-sensitised photo-oxidation of 2-methylpyrrole and 2,5-dimethylpyrrole and the isolation of new types of products from the latter. Except in one instance, analogous structures have not been reported in the parallel 2-methyl- and 2,5-dimethyl-furan photo-oxidation studies.[7,8]

The photo-oxygenation reaction was carried out in a water-cooled immersion apparatus containing a dilute (1·2 mmol %) methanolic solution of either 2,5-dimethylpyrrole (1) or 2-methylpyrrole (2)[9] and 2 mg % of Rose Bengal ($^1O_2$ sensitiser). A slow stream (30 ml/min) of oxygen was bubbled through the reaction vessel during an irradiation† period of 6 h. Precipitated platinum black[10] (35—45 mg) was added to destroy hydroperoxide (gas evolution observed), and methanol was evaporated from the photolysate *in vacuo*. After the photolysis of (1), column chromatography on silica gel (E. Merck, Darmstadt, 70—325 mesh ASTM) gave 35 wt % of a relatively non-polar fraction (EtOAc) and 65 wt % of a dark, highly polar fraction (MeOH). Preparative t.l.c. (Silica gel F, M. Woelm, Eschwege, 1 mm, diethyl ether) of the EtOAc fraction yielded three main components (3), (4), and (5); R_F 0·57, 0·20, and 0·12; theor. yield 9—12%, 5% and 6—7% respectively. Similarly (2) gave a 20% yield of (4) along with trace amounts of other as yet unidentified products. These reaction products from (1) or (2) are present even before the addition of platinum in the work-up (as determined by g.l.c.) The structures of (3), (4), and (5) were established by mass spectrometry and n.m.r. and i.r. spectrometry.



(1)



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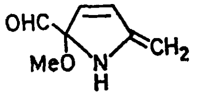

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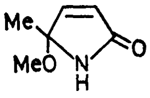

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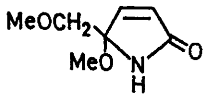
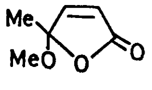


(5)



(6)

Maleimide as a photo-product from either (1) or (2) is formed in barely detectable amounts (no more than 0·1% yield), detection by t.l.c. or g.l.c. chromatography. This observation may be contrasted with the finding that another αα′-disubstituted pyrrole, 3,4-diethyl-2,5-dimethylpyrrole, gives a 20% yield of diethylmaleimide.[11] However, the already established photo-lability of maleimide (as compared with that of diethylmaleimide) under our reaction conditions[4] makes it unlikely to be formed in sufficient quantities to allow for isolation after the photo-oxygenation of (1) or (2) in the probable event that it is formed during the course of reaction.

The formation of (4) from either (1) or (2) might be rationalized (Scheme) by methanolysis of *endo*-peroxide (7) to form the hydroperoxide (8) which in turn decomposes to (4) in the reaction mixture. A completely analogous scheme has been postulated to account for the formation

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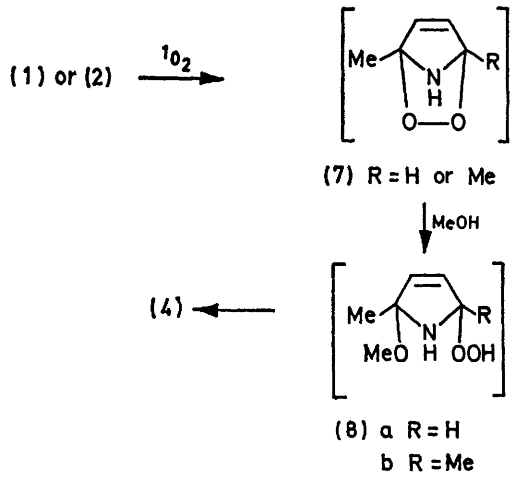
† Westinghouse tungsten-halogen quartz lamp, 120 v, 500 w, No. 500 Q/CL, run at 5 v.

of the pseudo-ketone (6) from 2-methylfuran.[7,8] However, although a hydroperoxide analogous to (8b) has been isolated after the dye-sensitised photo-oxygenation of 2,5-dimethylfuran, it has not been reported to undergo the demethylation reaction [to form (6)] that we have observed in the photo-oxidation of (1).[12] Dealkylative decompositions of hydroperoxides have been noted by others; however, strong acid catalysts is usually necessary.[13] We believe that the decomposition of (8a) or (8b) to form (4) occurs as a thermal reaction at room temperature during photolysis or evaporation of methanol solvent but before treatment with platinum which would have reduced (8b) to 2-hydroxy-5-methoxy-2,5-dimethyl-Δ^3-pyrroline.[7]



Scheme

In the light of what is known of the structures of the products from the photo-oxidation of phenylated pyrroles,[6] other alkylpyrroles[1,4] and alkylfurans,[8,7] the formation of (3) and (5) from (1) was completely unprecedented. They represent the first reported examples of photochemical oxidation at the α-alkyl carbon of pyrroles or furans. We suspect that in each instance two photo-oxidative steps are involved; however, it is premature to speculate on potential mechanisms. The mechanistic details of these reactions and an analysis of the more polar chromatographic fraction (MeOH) are currently under investigation in our laboratory.

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