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The Photosensitised Oxygenation of 3-Methylpyrrole involving a Dioxetan Intermediate[1]

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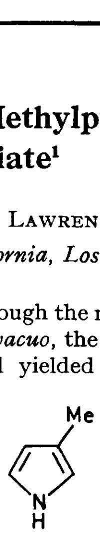
Summary The dye-sensitised photo-oxygenation of 3-methylpyrrole in methanol gives 3-methyl-3-methoxy-Δ^4-pyrrolin-2-one and 3-hydroxy-3-methyl-Δ^4-pyrrolin-2-one (which we assume arise *via* a dioxetan intermediate) as well as 3-methyl-5-methoxy-Δ^3-pyrrolin-2-one, 4-methyl-5-methoxy-Δ^3-pyrrolin-2-one, 5-hydroxy-3-methyl-Δ^3-pyrrolin-2-one, and citraconimide.

Until very recently,[2,3] the dye-sensitised photo-oxygenation of *C*-alkylated pyrroles had been largely uninvestigated. Except for the pioneering work of de Mayo and Reid[4] in their structure determination of the photo-oxidation products from pyrrole itself and *N*-ethylpyrrole, other investigations of pyrrole photo-oxygenation were essentially confined to various phenyl-substituted pyrroles.[5] Since virtually all known photo-oxidation products of pyrroles[2,4] and alkylpyrroles[2,3,6] appear to originate from *endo*-peroxide intermediates resulting from 1,4-cycloaddition of singlet oxygen at the α-carbons, oxygenation at a β-carbon in 3-methylpyrrole is unusual. This type of reaction, leading to (**2**) and (**3**), as well as an apparent substituent effect on the methanolysis of *endo*-peroxide (**8**) yielding nonequal amounts of (**4**) and (**5**), has not heretofore been observed.

A dilute (1·7 mmol) methanolic solution of 3-methylpyrrole (**1**)[7] containing 2·5 mg % of rose bengal ($^1O_2$ sensitiser) was photolysed† in a water-cooled Pyrex immersion apparatus for 6 h while a slow stream of oxygen was bubbled through the reaction vessel. After evaporation of methanol *in vacuo*, the photolysate was chromatographed on silica gel and yielded six components (60 weight % of the total photolysate) in the ethyl acetate fractions. Separation was achieved by preparative thin layer chromatography to yield (**2**)—(**7**) (yields 3, 6, 22, 7, 10, and 13% respectively).



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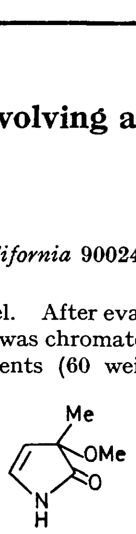

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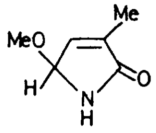

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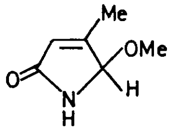

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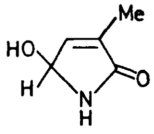

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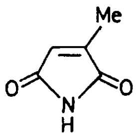

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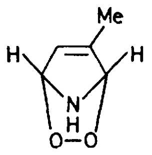

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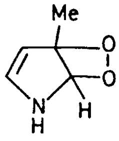

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† Westinghouse tungsten-halogen quartz lamp, 120 V, 500 W, No. 500 Q/CL, run at 50 V.

The structures were characterized by a combination of spectroscopic methods and [in the case of (**7**)] also by comparison of its m.p. with that of an authentic sample.

The reaction of (**1**) to form (**2**) and (**3**) constitutes the first example of photo-oxygenation at a pyrrole β-carbon unaccompanied by disruption of the pyrrole ring.[6] The formation of both (**2**) and (**3**) might occur from a common dioxetan intermediate (**9**) arising from 1,2-cycloaddition of singlet oxygen[8] to the enamine-like 2,3-bond of 3-methylpyrrole. We could find no analogous products involving C-4 of (**1**). We assume that products (**4**), (**5**), (**6**), or (**7**) are formed from *endo*-peroxide (**8**) after 1,4-addition of $^1O_2$.[9] We cannot as yet account for the unequal percentage yield of the isomeric methoxylactams (**4**) and (**5**) which favours (**4**) by a factor of 3. So far we have observed hydroxylactam structures such as (**6**) only after photo-oxygenation of pyrroles with one α-alkyl substituent,[1,3] but the direct formation of imides, *e.g.* (**7**), has been well established.[2,3,6] The mechanistic details of these reactions are being studied.

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[1] For preceding paper on Pyrrole Photo-oxidation Studies, see D. A. Lightner and L. K. Low, *J. Heterocyclic Chem.*, 1972, **9**, 167.

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[6] Cleavage of the 2–3 bond of 2,3,4,5-tetraphenylpyrrole has been reported in reference 5 (a). We have observed a similar reaction in the photo-oxygenation of 3,4-diethyl-2,5-dimethylpyrrole leading to 5-acetamido-4-ethyl-hex-4-en-3-one, and even a further photo-oxidation leading to *N*-acetylacetamide, D. A. Lightner and G. B. Quistad, *Angew. Chem.*, 1972, 216.

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