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SENSITIZED PHOTOOXIDATION
OF N-METHYLPYRIDINIUM-3-OXIDE AND ITS RELATED COMPOUNDS

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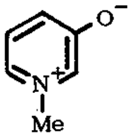
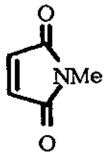
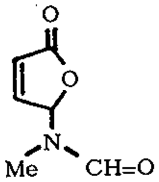
In connection with our previous observation which indicated the involvement of a peroxirane intermediate, a dipolar species, in the sensitized photooxidation of a spirocyclic vinylcyclopropane derivative, we have now carried out the oxidation with N-methylpyridinium-3-oxide (I), a betaine, for the first time. The results, which show that there is a marked solvent effect on the product formation, are presented together with a discussion of the mechanism of their formation. When a chloroform solution of (I) was irradiated by means of a tungsten lamp under an oxygen atmosphere, 5-(N-methylformamido)-2(5H)furanone (II) was obtained along with N-methylmaleimide (III). On the other hand, the oxidation in an ethanol solution of (I) afforded diethyl maleate (IV), diethyl fumarate (V), N-methyl-3-hydroxy-α-pyridone (VI) and ethyl N-methyloxamate (VII). The formation of (II) was explained by lactonization after cleavage of the dioxetane intermediate; while (III) was produced by a further oxidation *via* the five-membered peroxide. In contrast to this, the reaction in a protic solvent is more complicated; none of the products correspond to an oxidation product formed with one molar unit of singlet oxygen, *i.e.*, (VI) has a lower oxidation state than the normal product, while the others formed by a multistep oxidation. The formation of (VI) can be interpreted in terms of intermolecular intervention of a dioxetane precursor, peroxirane, by reduction with solvent. A tentative pathway (path b) leading to (IV), (V) and (VII) has been proposed after excluding an alternative route by a further irradiation of (VI) which failed to give any isolable product.



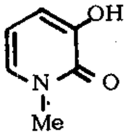
(I)



(III)



(II)



(VI)