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4,5-DIAZA-1,2-BENZOQUINONE DI-*N*-OXIDES

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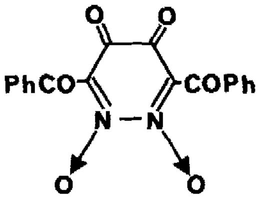
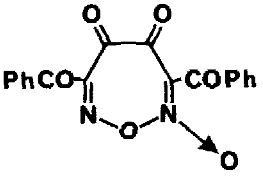
In a recent paper[1] it was indicated that some reactions of dimethyl 2,5-bis(diazo)-3,4-diketoadipate appear to proceed *via* formation of a 4,5-diaza-1,2-benzoquinone. The only compounds to which this type of structure has been assigned were obtained[2] by reaction of dinitrogen tetraoxide with, for example, 1,6-diphenylhexan-1,3,4,6-tetraone. The extensive degradative studies reported do not serve to distinguish between structures (I) and (II) for this orange-coloured compound.


I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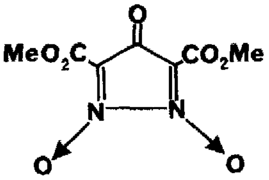
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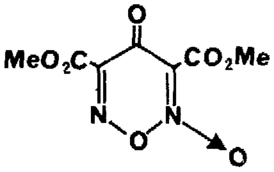
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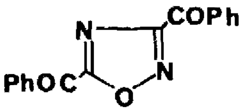
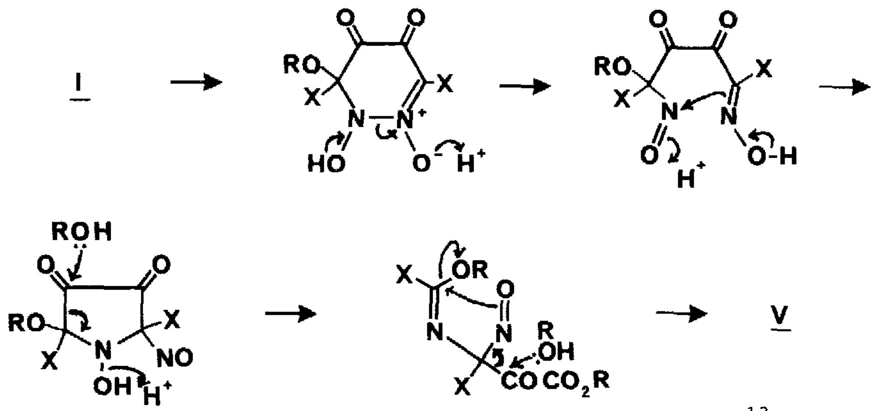

V

The proton-decoupled ^{13}C n.m.r. spectrum shows only the seven lines expected for structure (I) at 184.7 ($\underline{C}$ O), 168.3 ($\underline{C}$:O), 121.5 ($\underline{C}$-3), 137.2, 134.3, 131.0, and 130.6 (benzenoid $\underline{C}$ atoms) p.p.m. For comparison 3,4-dibenzoylfuroxan shows, *inter alia*, lines at 183.4 ($\underline{C}$.O), 181.8 ($\underline{C}$·O), 155.3 ($\underline{C}$-4) and 113.5 ($\underline{C}$-3) p.p m A similar problem in differentiating between structures (III) and (IV) for the products of oxidation of methylene ketones by nitrous acid is also elegantly resolved by ^{13}C n.m.r. spectroscopy. For example the product from dimethyl 1,3-acetonedicarboxylate[3] shows four lines at 167.8 ($\underline{C}$ O), 145.2 ($\underline{C}$.O), 89.5 (C-3, C-5) and 53.0 ($\underline{C}H_3$) p p.m. thus confirming the fairly recently proposed[4] formulation (III, R= CO_2CH_3).

Of particular interest to us was the described reaction[2] of (I) with alcohols leading to the corresponding dialkyl oxalate and the 3,5-dibenzoyl-1,2,4-oxadiazole (V). The latter structural assignment was arbitrary and it seemed equally likely that it could be a dibenzoyl-1,3,4- or 1,2,5-oxadiazole. The correctness of the original assignment, however, is indicated by the ^{13}C n.m.r spectrum, which shows eleven resolved lines rather than the six expected for the symmetrical isomers. The peaks at 184.2, 179.4, 171.8 and 167.0 p.p.m. are assignable to the carbonyl and oxadiazole ring carbon atoms. The structure of (V) was confirmed by an alternative preparation[5], albeit in low yield (ca. 10%), by refluxing a toluene solution of benzoyl cyanide and α-chloroisonitrosoacetophenone.

The obvious route to the dibenzoyloxadiazole (V) is by cycloaddition of benzoyl cyanide N-oxide to benzoyl cyanide and, indeed, the alcoholysis of (I) into these compounds is readily formulated. However, treatment of α-chloroisonitrosoacetophenone and benzoyl cyanide with triethylamine in ethanol did not give (V). Ethanolysis of (I) in the presence of a large excess of acrylonitrile[5,6] or phenylacetylene[6,7] failed to give the known benzoyl cyanide N-oxide adducts. Further, ethanolysis of the decadeutero analogue of (I) in the presence of a large excess of benzoyl cyanide gave solely the decadeutero analogue of (V). Hence the conversion of (I) to (V) must be intramolecular. Several mechanisms can be envisaged for this transformation and one of these is summarised in Scheme I.

Scheme I



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