Trapping a Nitroso-compound formed by Reduction of a Nitro-compound with Triethyl Phosphite

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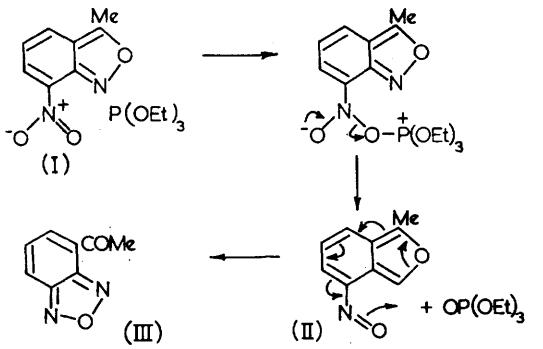
THE reduction of nitro-compounds with trivalent phosphorus derivatives has been used to prepare a variety of cyclised products;[1–5] the possibility of a nitrene intermediate, R·N:, prior to cyclisation has been the subject of considerable debate.[2,4,5] The reduction may involve a nitroso-intermediate (nitroso-compounds are also deoxygenated by phosphite[6]), or alternatively cyclisation may proceed with a phosphite–nitro-group adduct, with subsequent further deoxygenation of the product.[4] We present here evidence supporting the former hypothesis, in the isolation (in 60% yield) of 4-acetylbenzofurazan† (III) by phosphite reduction of 3-methyl-7-nitroanthranil (I). The simplest interpretation of this result is by the scheme depicted. We have shown previously[7] that the nitrosation of 5-dimethylaminobenzofuroxan gives 4-dimethylamino-7-nitrobenzofurazan: as tertiary aromatic amines are well known to be *C*-nitrosated, this indicates that nitroso-compounds of type (II) may undergo smooth rearrangement of type (II → III).

The only previous evidence of a nitroso-intermediate in the phosphite reduction of a nitro-compound is the isolation of phenylacetonitrile by



reduction of 1-nitro-2-phenylethane, and demonstration that phenylacetaldehyde oxime under the same reaction conditions forms the same nitrile.[5]

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† I.r., u.v., and n.m.r. spectra, and analytical data supported the structure (II) assigned to the product.

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