

A New Ring-opening Reaction of Strained Furoxans

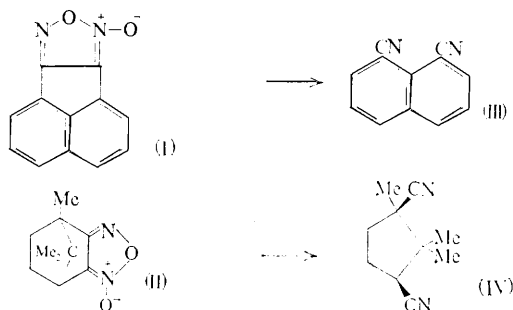
By ALTAF-UR-RAHMAN and A. J. BOULTON*

(School of Chemical Sciences, The University of East Anglia, Norwich, NOR 85C)

FUSION of the furoxan (1,2,5-oxadiazole-2-oxide) nucleus to a five-membered ring apparently gives rise to an unfavourable situation, due to ring strain.¹ The only known compounds to contain this system are the long-known acenaphthylene² and camphor³ derivatives (I) and (II). These two compounds are both liable to decompose violently at or about their melting points,† and attempts to prepare their furazan analogues have failed.¹

Since trialkyl phosphites have proved to be efficient reagents for the deoxygenation of furoxans to furazans,⁴ the reduction of (I) and (II) with trimethyl phosphite was studied. We have found that this reaction proceeds anomalously, to give the dinitriles (III) and (IV) in good yields. Nitrile oxides are probable intermediates; these

compounds have been shown to be reduced to nitriles very rapidly by phosphite.⁵



(Received, December 7th, 1967; Com. 1307.)

† Observations of the present Authors. Other furoxans are stable to fairly high temperatures.

¹ J. H. Boyer, in "Heterocyclic Compounds", ed. R. C. Elderfield, I. Wiley, New York, 1961, p. 462.

² F. M. Rowe and J. S. H. Davies, *J. Chem. Soc.*, 1920, **117**, 1344. The "*ψ*-*o*-dinitroso-" structure suggested for this compound in reference 1 is no longer accepted.

³ M. O. Forster, *J. Chem. Soc.*, 1903, **83**, 514.

⁴ T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, 1962, **27**, 3651; C. Grundmann, *Chem. Ber.*, 1964, **97**, 575; A. S. Bailey and J. M. Evans, *Chem. and Ind.*, 1964, 1424.

⁵ C. Grundmann and H.-D. Frommelt, *J. Org. Chem.*, 1965, **30**, 2077.