Tetrahedron Letters No. 30, pp 2821 - 2822.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0722-2821$02.00/0

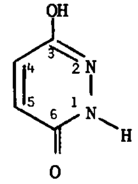
AN E.S.R. STUDY OF RADICALS OBTAINED BY THE OXIDATION OF 3,6-DIHYDROXYPYRIDAZINES

Dolores M. Holton, Patricia M. Hoyle and David Murphy*

Department of Chemistry, Bedford College, Regent's Park, London NW1 4NS

One electron oxidation of the plant growth substance 3,6-dihydroxypyridazine (maleic hydrazide) gives a cyclic α-carbonylhydrazyl, the e.s.r. parameters of which are assigned by comparison with five related radicals.

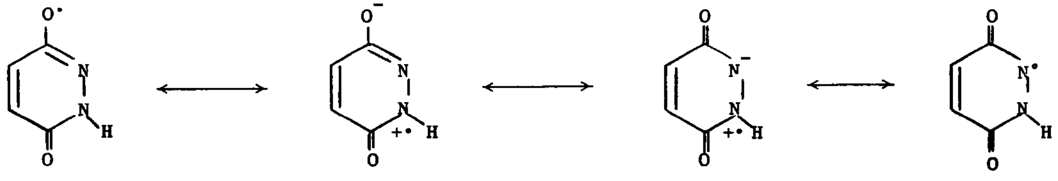
3,6-Pyridazinedione[1] is one of a growing number of cyclic α-carbonylazo-compounds investigated in the search for highly reactive dienophiles which have proved most valuable in the synthesis of difficultly accessible ring systems. The diazaquinone is conveniently prepared by the reaction of the potassium salt of 3,6-dihydroxypyridazine (maleic hydrazide) with t-butyl hypochlorite in acetone at -78°C. In this work, the one electron oxidation of the hydrazide has been studied by e.s.r. spectroscopy in order to determine the nature of any radical intermediates.



(1)

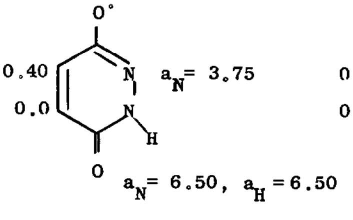
Maleic hydrazide exists almost entirely in the monolactim form (1). Oxidation of a 5 x 10^{-3} mol dm^{-3} solution of (1) with 5 x 10^{-3} mol dm^{-3} cerium(IV) sulphate in 0.1 mol dm^{-3} sulphuric acid using a flow system[2] resulted in an intense e.s.r. spectrum, splittings 3.75 (1N), 6.50 (1N), 6.50 (1H) and 0.40 x 10^{-4} T (1H). As these values cannot be unambiguously assigned, a series of substituted derivatives of (1) were prepared and examined in a similar way; the results are given in the table, radicals (2)-(7). It has been demonstrated[3] that in a large number of radicals containing N-H groups, $a_N \approx a^{H}_{NH}$, so that the observed splittings can be assigned as in (2)-(7).

The stability of the radicals as indicated by the intense e.s.r. signals is due to delocalisation as in (2a)-(2d). Studies of other α-carbonylhydrazyl radicals[4] have suggested

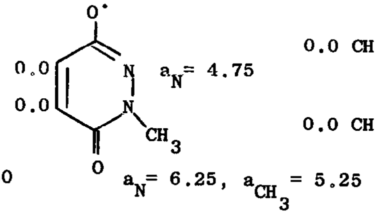


(2a) (2b) (2c) (2d)

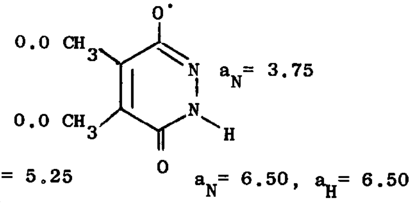
Table 1. E.s.r. parameters ($a/10^{-4}$ T) for radicals from 3,6-dihydroxypyridazines



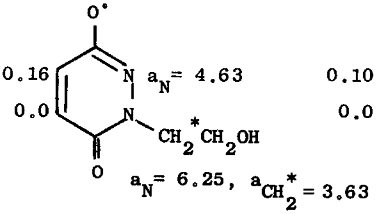
(2)



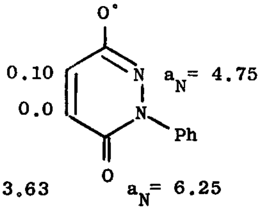
(3)



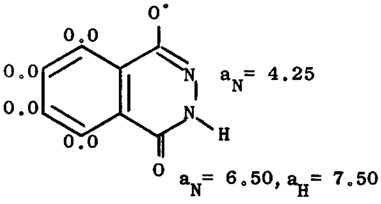
(4)



(5)



(6)



(7)

that in the presence of the carbonyl group, forms (*2b*) ⟷ (*2c*) with the unpaired electron mainly on N(1) are major contributors to the structure. Thus, in the experimental conditions used in this work (*2b*), which may be protonated in the acid solutions, is consistent with the observed splittings, with $a_{N(1)} > a_{N(2)}$.

Attempts to obtain diazasemiquinone by autoxidation of (*1*) in alkaline solution[5] were unsuccessful.

As it is shown that (*1*) is readily oxidised to give a free radical (*2*) it is possible that the plant growth inhibiting action[6] of (*1*) is connected with such an intermediate. The more stable, but related, bipyridinyl radicals are potent herbicides[7].

D.M.H. thanks the S.R.C., and P.M.H. thanks the University of London for research grants.

REFERENCES

1. T.J. Kealy, J. Amer. Chem. Soc., 1962, 84, 996.
2. W.T. Dixon and R.O.C. Norman, J. Chem. Soc., 1963, 3119
3. A.T. Bullock and C.B. Howard, Trans. Faraday Soc., 1970, 66, 1861
4. Y.M. Ryzhmanov, Y.V. Yablokov, B.M. Kozynev, L.I. Stashkov and R.O. Matevosyan, Doklady Chem., 1965, 162, 443
5. W.T. Dixon, P.M. Kok and D. Murphy, Tetrahedron Lett., 1976, 623
6. L.J. Audus, Plant Growth Substances, (Hill, London, 2nd Edn., 1959)
7. W.R. Boon, Endeavour, 1967, 26, 27; Outlook Agr., 1963 and refs. therein.

(Received in UK 14 May 1979)