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A COMPARISON OF THE DECOMPOSITION OF A 3-NITRENO-1,3-OXAZOLIN-2-ONE AND THE ISOMERIC 1,3,4-OXADIAZIN-2-ONE

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Summary: The oxidation of 3-amino-4,5-diphenyl-1,3-oxazolin-2-one (7) affords monodiazobenzil 10 as the primary decomposition product of N-nitrenolactam 1. In contrast, the oxidation 3,6-dihydro-5,6-diphenyl-1,3,4-oxadiazin-2-one (6) leads to diphenylacetylene (12) via oxadiazin-2-one 2.

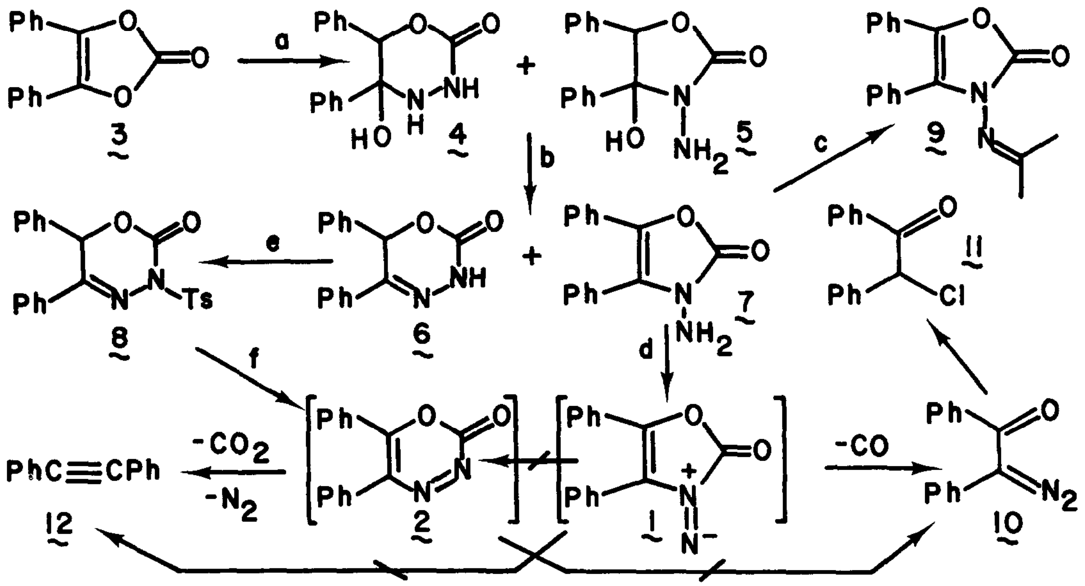
Simple 1,1-diazenes (nitrenoamines) tend to either dimerize to tetrazenes or lose nitrogen much more readily than their 1,2-diazene (azo alkane) analogues.[1,2] We wish to report the preparation of the nitrenolactam 1 and its azo analogue 2, and the striking contrast in the thermal decomposition of these two isomers.

Addition of N_2H_4 to diphenylethylene carbonate (3)[3] quantitatively affords a mixture of 4 and 5 which are dehydrated smoothly to form a mixture of the novel heterocycle 6 (46%) and 7 (45%). Upon separation by silica gel chromatography, 6 had mp 187-189°C (dec) and its N-tosyl derivative 8, mp 156.6-157.0°C (56%), while 7 had mp 131.5-131.6°C and it hydrazone derivative from acetone 9, mp 105-106°C.[4]

The oxidation of 6 and 7 was examined under a variety of conditions. Oxidation of 7 with t-BuOCl-Et_3N at -78°C gives rise to a transient (∿1 min) deep blue color.[1b,d] While this observation implies the transient presence of a 1,1-diazene such as 1 no products could be isolated and attempted aziridine formation in olefin-trapping experiments was unsuccessful.[5,6] On the other hand, PCC oxidation of 7 yields either monodiazobenzil (10, 60%, CH_2Cl_2, 0°C) as the primary oxidation product or desylchloride (11, 70%, CH_2Cl_2, R.T., 6 hr.) from reaction of 10 with HCl sources in the reaction mixture. In contrast 6 is not readily oxidized by these reagents, but its N-tosyl derivative 8 does undergo a smooth elimination of toluene sulfinate to form diphenylacetylene (12, 40%) as the only isolable product.

These reactions are most easily rationalized as proceeding through the labile nitrenolactam 1 in the case of 7 and the azo lactone 2 in the case of 8. Apparently, 1 extrudes carbon monoxide to yield 10,[7] and 2 extrudes both carbon dioxide and nitrogen to form 12. The mutually exclusive formation of 10 and 12 indicate that the known ring expansion mode, 1 → 2,[5a,8] and the alternative extrusion modes, 1 → 12 and 2 → 10, do not occur. Since extrusion modes 1 → 10 and 2 → 12 are symmetry allowed and modes 1 → 12 and 2 → 10 are symmetry forbidden, the simplest interpretation of these results is that the decomposition of 1 and 2 are orbital symmetry-controlled, concerted processes. This correlation may be of substantial value in the rational design of diazene-based cycloreversions where either the carbon monoxide or carbon dioxide extrusion mode may be the desired process.

Scheme



a) N_2H_4; b) P_2O_5; c) acetone; d) PCC; e) NaH,TsCl; f) t-BuLi, -78°C

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4. All new substances reported here gave satisfactory elemental analyses and had spectroscopie properties in accord with the proposed structures: 6 had IR ($CDCl_3$) 3600-3100, 1760 cm^{-1}; NMR ($CDCl_3$ δ) 8.5 ppm (bs, 1H), 7.2-7.8 (m, 10H), 6.4 (s, 1H); m/e M$^+$252 and 7 had IR ($CDCl_3$) 3000, 1750cm^{-1}; NMR ($CDCl_3$, δ) 7.5 ppm (s, 5H), 7.1-7.5 (m, 5H), 4.3 (s, 2H, D_2O exchangeable); m/e M$^+$252.
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