Modified Photochemical Reactivity Arising from Homoconjugative Interaction with an Azoxy-system

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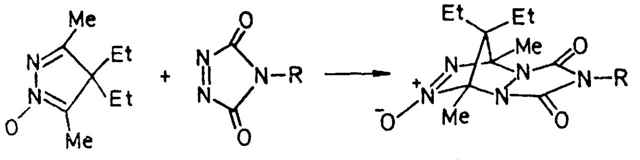
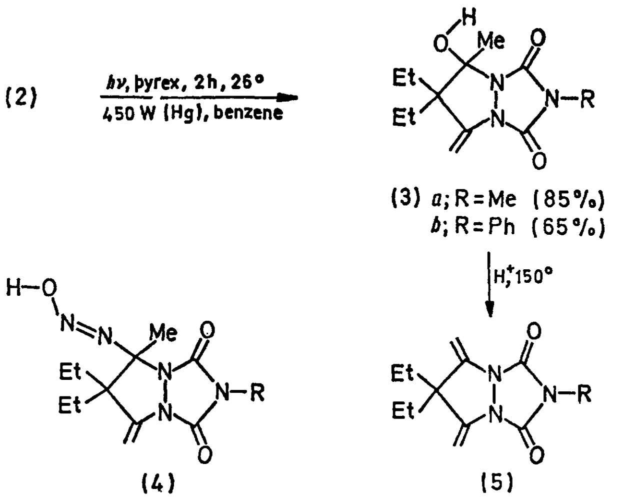
Summary The photochemical behaviour of bicyclic azoxy-compounds is strongly influenced by the presence of cross-ring, non-bonded nitrogens, which apparently are capable of homoconjugative interaction with the reactive excited state of the azoxy-chromophore.

Bicyclic azoxy-compounds, (**2a**) and (**2b**) were prepared almost quantitatively by the previously unreported reaction[1] shown below. This reaction is analogous to a number of other reactions of potent dienophiles with azines.[2–5] Few photochemical studies of aliphatic azoxy-systems have been reported.[6–8]


(1) R = Me or Ph (2) *a*; R = Me
b; R = Ph

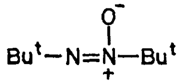
We report now a new type of photochemical transformation which may, under appropriate structural conditions, be undergone by azoxy-compounds. The reaction may speculatively be envisaged as proceeding *via* an initial Type II process, perhaps producing (**4**) as an intermediate which could then undergo subsequent thermal or photochemical extrusion of N_2 followed by cage recombination to give the alcohol product (**3**).

Compound (**3**) could be converted thermally, under acid catalysis at 150°, into the diene (**5**). Interestingly, the azoxy-compounds (**2a**) and (**2b**) were themselves thermally labile, being converted in 85% yield into the dienes (**5a**) and (**5b**) in $CHCl_3$ or EtOH under reflux with no acid catalysis. The photoproduct (**3**) was stable indefinitely under these conditions, thus indicating that the thermal process most likely did not proceed *via* the intermediacy of this alcohol An indication that the thermal transformation of (**2**) into (**5**) is not a simple unimolecular process analogous to an amine oxide elimination, was the fact that (**2**) could be refluxed in Me_2SO for many hours without significant decomposition.



(3) *a*; R = Me (85%)
b; R = Ph (65%)
(4) (5)

The expectation that this photochemical reaction might prove to be generally observable where azoxy-species have β-hydrogens or possibly for other similarly constrained bicyclic azoxy-compounds, however, was not confirmed. The azoxy-t-butane, (**6**), under comparable photolysis conditions produced neither isobutylene nor t-butyl alcohol, while the bicyclic azoxy-species (**7**) and (**8**) rapidly polymerized upon irradiation with no monomeric photoproducts being produced, thus exhibiting behaviour very similar to that of (**9**). Such behaviour contrasted sharply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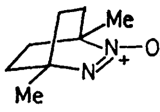
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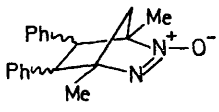
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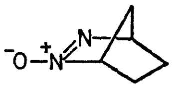
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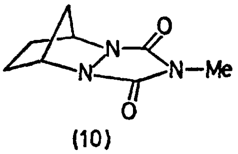
(10)

with the relatively slow and clean transformations observed for (**2a**) and (**2b**).

The conclusion that is demanded from this study is that the cross-ring nitrogens of (**2**) are vital to the ability of this photochemical reaction to proceed. There is indeed, some indication that these nitrogens give rise to a perturbation of the $n \rightarrow \pi^*$ excited state of the azoxy-chromophore. Unlike the simple azoxy-compounds, (**7**) and (**9**) which show absorptions at λ_{max} 230 and 287 nm (ϵ 6420 and 70) and at 228 nm (ϵ 6000), respectively, (**2a**) has a longer wavelength, more intense $n \rightarrow \pi^*$ transition, λ_{max} 314 (ϵ 830) as well as its normal intense $\pi \rightarrow \pi^*$ transition, λ_{max} 231 nm (ϵ 7220). The simple urazole system such as contained in (**10**) cannot alone account for this new absorption since (**10**) has λ_{max} at 227 nm (ϵ 3826). Such so-called homoconjugative interactions in bicyclic systems have been reported previously for cross-ring interactions of nitrogens with olefinic and azo-bonds.[2,9–11] There have also been reports of transannular charge-transfer-type interactions (*e.g.* between S and carbonyl) which lead to drastic modifications in reaction paths.[12] However there is no spectroscopic evidence in our systems for charge-transfer transitions, nor would they be expected since nitrogen should be essentially no more polarizable than oxygen as a substituent and oxygen has been shown to be ineffective as an electron donor in potential charge-transfer situations.[12] Thus at present, the vague explanation of this special reactivity must be that it results from an as yet ill-defined perturbation of the $n \rightarrow \pi^*$ excited state of the azoxy-chomophore. While such cross-ring perturbations by nitrogen have been observed before, our results, for the first time, implicate such interactions as causing a change in reactivity.

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[1] H. Gnichtel and J. J. Schonherr, *Chem. Ber.*, 1966, **99**, 618.
[2] A. B. Evnin and D. R. Arnold, *J. Amer. Chem. Soc.*, 1968, **90**, 5330.
[3] A. B. Evnin, A. Y. Lam, J. J. Maher, and J. J. Blyskal, *Tetrahedron Letters*, 1969, 4497.
[4] W. Dittmar, G. Heinrich, A. Steigel, T. Troll, and J. Sauer, *Tetrahedron Letters*, 1970, 1623.
[5] L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, 1970, **92**, 1965.
[6] B. G. Gowenlock, *Canad. J. Chem.*, 1964, **42**, 1936.
[7] F. D. Greene and S. S. Hecht, *J. Org. Chem.*, 1970, **35**, 2482.
[8] K. Grant Taylor, *J. Amer. Chem. Soc.*, 1972, **94**, 250.
[9] J. Parello, A. Melera, and R. Goutarel, *Bull. Soc. chim. France*, 1963, 898.
[10] J. Wagner, W. Wojnarowski, J. E. Anderson, and J. M. Lehn, *Tetrahedron*, 1969, **25**, 657.
[11] B. T. Gillis and R. A. Izydore, *J. Org. Chem.*, 1969, **34**, 3181.
[12] A. Padwa and A. Battisti, *J. Amer. Chem. Soc.*, 1972, **94**, 521.