

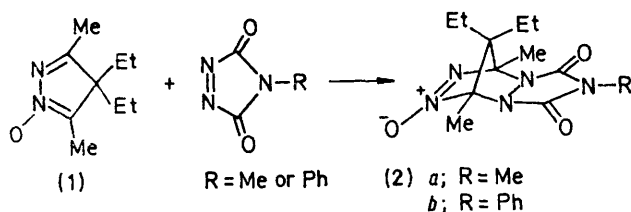
Modified Photochemical Reactivity Arising from Homoconjugative Interaction with an Azoxy-system

By WILLIAM R. DOLBIER, JUN,* W. DAVID LOEHLE, and W. MICHAEL WILLIAMS

(Department of Chemistry, University of Florida, Gainesville, Florida 32601)

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.

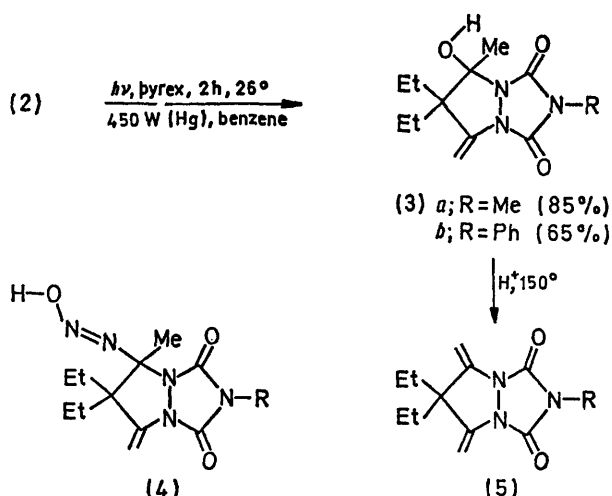
BICYCLIC azoxy-compounds, (2a) and (2b) were prepared almost quantitatively by the previously unreported reaction¹ shown below. This reaction is analogous to a number of other reactions of potent dienophiles with azines.²⁻⁵ Few photochemical studies of aliphatic azoxy-systems have been reported.⁶⁻⁸



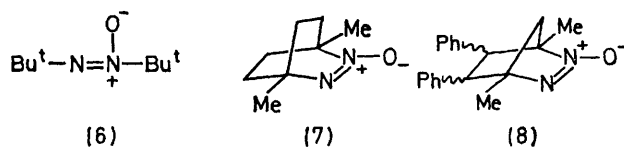
We report now a new type of photochemical transformation which may, under appropriate structural conditions, be undergone by azoxy-compounds. The reaction may speculatively be envisaged as proceeding *via* an initial Type II process, perhaps producing (4) as an intermediate which could then undergo subsequent 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.

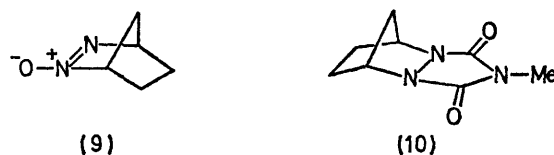
The expectation that this photochemical reaction might



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 photo-products being produced, thus exhibiting behaviour very similar to that of (9). Such behaviour contrasted sharply



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-chromophore. 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.

(Received, 18th April 1972; Com. 652.)

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. Parelo, 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.