The Photolysis of Azine Monoxides.[1] The Photorearrangement of a Non-aromatic Five-membered-ring Heterocycle

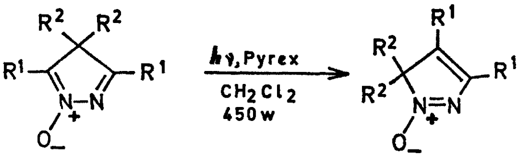
By WILLIAM R. DOLBIER, JUN.,* and W. MICHAEL WILLIAMS

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

Summary The photochemical rearrangement of 4,4-dimethyl-3,5-diphenyl-4*H*-pyrazole 1-oxide to 5,5-dimethyl-3,5-diphenyl-5*H*-pyrazole 1-oxide is reported.

THERE is much current interest in the photochemical rearrangements of five-membered-ring heterocycles. Many aromatic systems are believed to isomerize by way of a ring-contraction ring-expansion sequence.[2] Singh and Ullman have, for example, presented good evidence for such a process being involved in the photorearrangement of 3,5-diarylisoxazoles to 2,5-diaryloxazoles *via* 3-aroyl-2-aryl-1-azirines. That an alternative pathway, involving an initial electrocyclic process, also exists for such systems has been suggested by the groups of Beak[3] and Tiefenthaler.[4] We report a new example of a photorearrangement of the latter type. This work provides the first example of a non-aromatic heterocycle undergoing this general type of rearrangement.

When 4,4-dimethyl-3,5-diphenyl-4*H*-pyrazole 1-oxide (**1a**) is irradiated, a single isomeric species is produced in 70% yield. 5,5-Dimethyl-3,4-diphenyl-5*H*-pyrazole 1-oxide, (**2a**) has been assigned as the product based upon its spectral and chemical properties, as well as an independent synthesis.



(1a) R^1 = Ph, R^2 = Me
(b) R^1 = Me, R^2 = Et

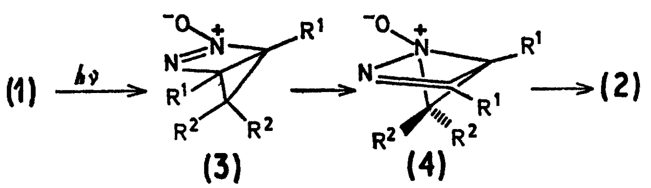
(2)

The mass spectrum and an elemental analysis indicated the isomeric nature of the product. A dominant i.r. peak at 1495 cm^{-1} and u.v. maxima (EtOH) at 337 (ϵ 4430) and 248 nm (ϵ 20,300) were indicative of the unsaturated azoxy-structure.[5] The ^1H n.m.r. spectrum with a sharp singlet at δ1·56 (6H) and a multiplet at δ 7·15—7·52 p.p.m. (10H), as well as the ^{13}C n.m.r. spectrum which showed two different phenyl groups, three different ring carbons, and two identical methyl carbons,† were consistent with the structure.

Photoproduct (**2a**) could be reduced quantitatively by $LiAlH_4$ in ether to 5,5-dimethyl-3,4-diphenyl-2-pyrazoline [u.v. (EtOH) λ_{max} 291 nm (ϵ 10,260)], which could be synthesized independently by treatment of 3-methyl-1,2-diphenylbut-2-en-1-one with hydrazine.

The above data while being consistent with structure (**2a**) do not exclude the possibility that the photoproduct may be the isomeric 2-oxide structure. To elucidate this possibility, (**1b**) was found to be converted photochemically in 29% yield into a compound which was assigned the structure (**2b**). The assignment of the 1-oxide structure was based upon its u.v. spectrum [λ_{max} 315 (ϵ 3530), 227 nm (ϵ 2380)] which was virtually identical to that of a very similar compound, 3,4,5,5-tetramethyl-5*H*-pyrazole 1-oxide, which had been studied by J. P. Freeman.[6] He found that the analogous 2-oxide had a very different u.v. spectrum [λ_{max} 241 nm (ϵ 6300)].

A reasonable mechanism can be suggested which gives rise to the 1- but not the 2-oxides. The initial, photochemical step is analogous to the electrocyclic reaction which we observed earlier for a seven-membered-ring azine oxide.[1] The second step can be thought of as a type of cyclopropylmethyl rearrangement which has analogy with Zimmerman's rearrangement observed in the 4,4-diphenylcyclohexadienone system.[7] Unlike other similar rearrangements in aromatic systems, the driving force of re-aromatization is not present here. The final step of the mechanism finds analogy in Closs' studies of the valence-bond isomerizations of 3*H*-pyrazoles.[8]



We acknowledge support of this work by the Petroleum Research Fund of the American Chemical Society.

(*Received, December 8th,* 1969; *Com.* 1856.)

---

† We thank Dr. Leroy Johnson of Varian Associates, Palo Alto, California, for running the ^{13}C n.m.r. spectrum of (2a).

[1] For previous part in the series, see W. R. Dolbier, jun., and W. M. Williams, *J. Amer. Chem. Soc.*, 1969, **91**, 2818.

[2] H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, 1967, **89**, 3501; B. Singh and E. F. Ullman, *ibid.*, p. 6911; H. Hiraoka and R. Srinivasan, *ibid.*, 1968, **90**, 2721.

[3] P. Beak and W. Messer, *Tetrahedron*, 1969, **25**, 3287; P. Beak, J. L. Miesel, and W. R. Messer, *Tetrahedron Letters*, 1967, 5315.

[4] H. Tiefenthaler, W. Dorscheln, H. Goth, and H. Schmid, *Helv. Chim. Acta*, 1967, **50**, 2244.

[5] C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *J. Amer. Chem. Soc.*, 1958, **80**, 6088.

[6] J. P. Freeman, *J. Org. Chem.*, 1962, **27**, 1309.

[7] H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, 1967, **89**, 906.

[8] G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, 1968, **90**, 173.