

Preparation and Thermal Rearrangement of a Benzofuran-Nitrene Adduct

By D W JONES

(Department of Organic Chemistry, The University, Leeds LS2 9JT)

Summary Addition of phthalimidoimidogen (phthalimidonitrene) to benzo[*b*]furan gives the benzofuroaziridine (2) which on heating rearranges to an isomer (5)

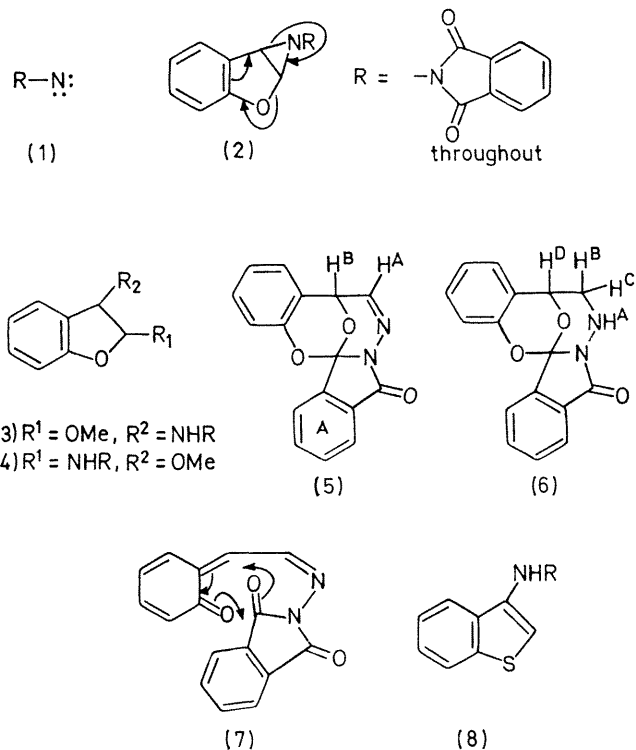
shift to that of a cyclic imine (τ 2.25)⁷ H^B resonates at τ 4.47 (d, *J* 3.5 Hz) Hydrogenation of (5) over platinum

THE addition of phthalimidonitrene (1) to olefins has provided a useful synthesis of aziridines¹ Since the nitrene is generated by lead tetra-acetate oxidation of *N*-amino-phthalimide at or below 0° the method should prove useful for the synthesis of aziridines which would decompose under the conditions required for the generation of most nitrenes²

In agreement, generation of phthalimidonitrene in the presence of benzo[*b*]furan gave the furoaziridine (2) (50%), m p 139—140°, ν_{\max} 1705 and 1760 cm⁻¹, the n m r spectrum indicated the expected³ slow inversion about nitrogen, the protons of the dihydrofuran ring appearing as 4 doublets The pair at τ 3.94 and 5.45 (*J* 4.5 Hz) correspond to one invertomer, and the pair at τ 4.1 and 5.34 (*J* 2.5 Hz) to an equal amount of the other

Chemical evidence for structure (2) is provided by reaction with methanol which affords a mixture of the methyl ethers (3) and (4) as well as an isomer of (2)

This isomer, m p 186—188°, is conveniently prepared by rearrangement of (2) in boiling toluene The structure (5) assigned to this compound is based on the following evidence The presence of CO absorption at 1725 cm⁻¹, and the absence of a band at 1760—1800 cm⁻¹ is consistent with a phthalimidine⁴ rather than a phthalimide derivative Similarly the n m r spectrum (CDCl₃) shows the ring A protons as an unsymmetrical signal at τ 2.2, rather than the symmetrical AA'BB' pattern characteristic of simple phthalimides This resonance obscures the resonance of H^A which as expected⁵ occurs at higher field than in related compounds of presumed *anti*-configuration (τ 1.0—1.7)^{1,6} and at a similar chemical



proceeded without hydrogenolysis, which is slow for α -aryl- β -amino-compounds,⁸ and gave (6), τ (CDCl₃-D₂O) 7.08

(1H, dd, J 13 and 1.5 Hz, H^B), 6.38 (1H, dd, J 13 and 3 Hz, H^C), and 4.8 (1H, dd, J 3 and 1.5 Hz, H^B). In the absence of D₂O the coupling of H^B and H^C with H^A (τ 5.8) is also apparent (J_{AB} 2.5, J_{AC} 13 Hz). The presence of a CH·CH₂·NH moiety in (6) and consequently of a -CH·CH=N- moiety in (5) is thus confirmed.

Possible mechanisms for the conversion of (2) into (5) include a ring-opening (2; arrows)† to the stabilised quinone-methide (7) and ring closure as indicated (7; arrows). Support

for the first step of this mechanism is provided by the reaction of phthalimidonitrene with simple furans which affords stable ring-opened products related to (7).⁹

In addition to *cis*-1,4-diphthalyltetrazene¹⁰ the reaction of phthalimidonitrene with benzo[*b*]thiophen gives the insertion product (8) identical to a sample prepared by condensing thioindoxyl with *N*-aminophthalimide; no aziridine was detected.

(Received, July 2nd, 1971; Com. 1119)

† Cf. the rearrangement of chloroaziridines (ref. 1).

¹ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576.

² E.g. K. Hafner and W. Kaiser, *Tetrahedron Letters*, 1964, 2185.

³ R. S. Atkinson and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 772; D. J. Anderson, R. S. Atkinson, and D. C. Horwell, *J. Chem. Soc. (C)*, 1971, 624.

⁴ Z. Ichi Horii, C. Iwata, and Y. Tamura, *J. Org. Chem.*, 1961, 26, 2273.

⁵ L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Oxford, 1969, p. 226.

⁶ R. E. Harmon, J. L. Parsons, and S. K. Gupta, *J. Org. Chem.*, 1969, 34, 2760.

⁷ Qui Khuong-Huu and A. Pancrazi, *Tetrahedron Letters*, 1971, 37.

⁸ R. L. Augustine, "Catalytic Hydrogenation", Arnold, London, 1965, p. 135.

⁹ D. W. Jones, unpublished observations.

¹⁰ D. W. Jones, *Chem. Comm.*, 1970, 1084.