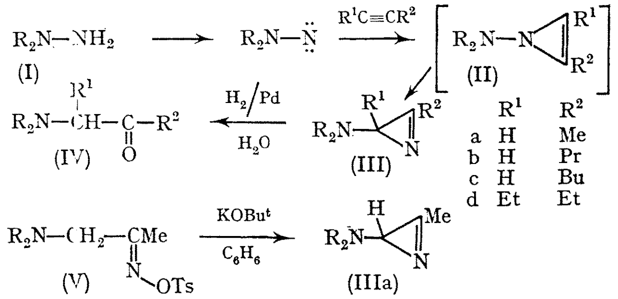
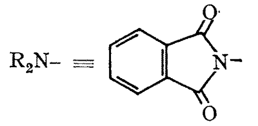
Addition of Nitrenes to Acetylenes. Anti-aromaticity of 1*H*-Azirines

By D. J. ANDERSON, T. L. GILCHRIST, and C. W. REES*

(*Department of Chemistry, University of Leicester, Leicester* LE1 7RH).

As a cyclic, planar 4π-electron system, isoelectronic with the cyclopropenyl anion, 1*H*-azirine could be destabilised by electron delocalisation; that is, it would be anti-aromatic.[1] This would explain why no 1*H*-azirine has yet been isolated or even clearly demonstrated to be a reaction intermediate.†





The addition of nitrenes to acetylenes is an obvious route to 1*H*-azirines but, so far, has failed to give azirines; for example, acylnitrenes give oxazoles by 1,3-dipolar cycloaddition.[2] Recently, the failure to generate 1*H*-azirines by elimination of hydrogen chloride from chloroaziridines has also been reported.[3] We now describe the first addition of a nitrene to acetylenes to give 1*H*-azirines and the spontaneous rearrangement of the latter to the 2*H*-isomers.

N-Aminophthalimide (I) is rapidly oxidised by lead tetraacetate in dichloromethane containing an olefin, at or below room temperature, to give *N*-phthalimidylaziridines.[4] Similar oxidation in the presence of hex-3-yne gave a 1 : 1 nitrene–acetylene adduct (oil; 15%); this was not the symmetrical 1*H*-azirine (IId), as was shown by the non-equivalence of the two ethyl groups in the n.m.r. spectrum, but the 2*H*-azirine (IIId). Prop-1-yne, pent-1-yne, and hex-1-yne gave similar nitrene adducts (*ca.* 5%), all with the 2*H*-azirine structures (IIIa, b, c). Evidence for these structures rests on the spectroscopic data, particularly n.m.r. and mass spectral fragmentation, on the quantitative conversion of (IIIb) (m.p. 46—47°) into the ketone (IVb) by catalytic hydrogenation in moist ethyl acetate (*cf.* ref. 5), and on the independent synthesis of (IIIa) (m.p. 130—131°, 30%) from the oxime toluene-*p*-sulphonate (V) and potassium t-butoxide in boiling benzene. The structure of the ketone (IVb) was confirmed by an independent synthesis from potassium phthalimide and 1-bromopentan-2-one.

In the 2*H*-azirines (III), the nitrogen lone-pair is in an sp^2 orbital orthogonal to the $p\pi$-orbital of the carbon–nitrogen double bond; the system is therefore no longer anti-aromatic but is non-aromatic. The very rapid rearrangement of the 1*H*-azirines, which are presumably formed first, to the 2*H*-azirines under such mild conditions strongly supports the high energy, anti-aromatic nature of the former. The mechanism of this novel rearrangement is under investigation.

(*Received, December 9th,* 1968; *Com.* 1680.)

---

† 1-Acetyl-1*H*-azirine-2-carboxylic acid has been reported as a product of the reaction of 1*H*-1,2,3-triazole-4,5-dicarboxylic acid with acetic anhydride (S. Yamada, T. Mizoguchi, and A. Ayata, *J. Pharm. Soc. Japan*, 1957, **77**, 452; *Chem. Abs.*, 1957, **51**, 14698b). We have repeated this reaction and have found that the spectral data and the m.p. (183—184°) of the product accord with those expected for the isomeric 2-methyloxazole-4-carboxylic acid (J. W. Cornforth and R. H. Cornforth, *J. Chem. Soc.*, 1947, 96). The data are inconsistent with a 1*H*-azirine structure.

[1] R. Breslow, *Angew. Chem. Internat. Edn.*, 1968, **7**, 565; R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, 1967, **89**, 4383.

[2] J. Meinwald and D. H. Aue, *J. Amer. Chem. Soc.*, 1966, **88**, 2849; R. Huisgen and H. Blaschke, *Chem. Ber.*, 1965, **98**, 2985.

[3] F. W. Fowler and A. Hassner, *J. Amer. Chem. Soc.*, 1968, **90**, 2875.

[4] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, preceding Communication.

[5] D. J. Cram and M. J. Hatch, *J. Amer. Chem. Soc.*, 1953, **75**, 33.