Formation of 2*H*-Azirines by the Pyrolysis of 1,2,3-Triazoles

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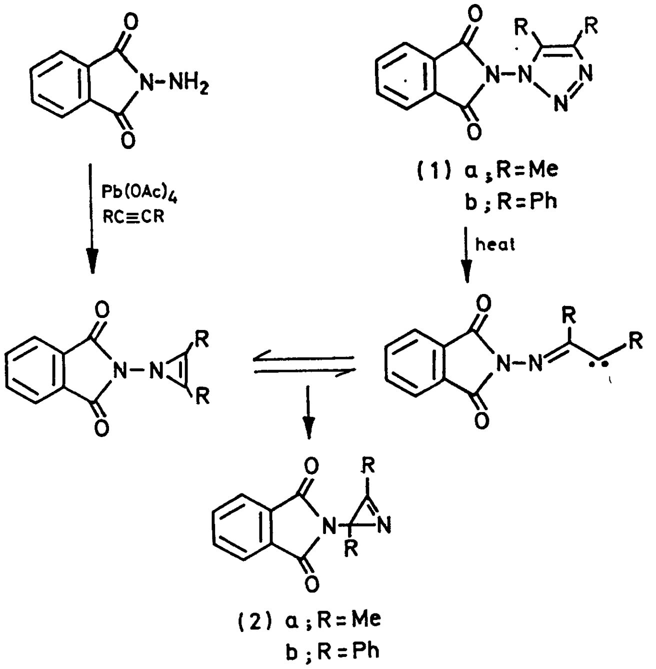
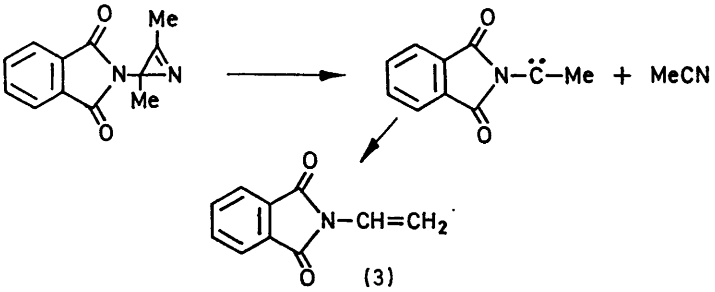
Summary 1-Phthalimido-1,2,3-triazoles (**1**) thermally fragment in the vapour phase; the products isolated are 2*H*-azirines (**2**) and compounds derived from these azirines by further fragmentation or rearrangement.

2*H*-AZIRINES (**2**) are the products isolated from the oxidation of *N*-aminophthalimide in the presence of alkynes.[1] In order to elucidate the mechanism of this reaction, we have studied the flash vacuum pyrolysis of 4,5-disubstituted-1-phthalimido-1,2,3-triazoles (**1**), on the basis that the triazoles could, by loss of nitrogen, give the same intermediates as are involved in the oxidation (Scheme 1). 2*H*-Azirines have now been isolated from the pyrolyses, showing that common intermediates are indeed probably involved in the oxidations and in the pyrolyses.



SCHEME 1

The triazoles (**1a**), m.p. 175·5—176·5°, and (**1b**), m.p. 189°, were prepared by condensation of the corresponding 1-aminotriazoles[2] with phthalic anhydride. The dimethyltriazole (**1a**) was pyrolysed by passage of the vapour through a glass tube (15 × 1 cm) at 450° and 0·02 mmHg, and the product mixture was analysed by n.m.r. Four products were identified, pure specimens of the solid products being obtained by chromatography of the mixture after n.m.r. analysis. The products were phthalimide (10%), 2,3-dimethyl-2-phthalimido-2*H*-azirine (**2a**) (10%), m.p. 78° (identical with a specimen obtained by the oxidation of *N*-aminophthalimide in the presence of but-2-yne), *N*-vinylphthalimide (**3**) (80%), and acetonitrile. The last two compounds were shown to be secondary products, derived from the azirine (**2a**) by fragmentation: the pure azirine, when subjected to the same reaction conditions, gave only *N*-vinylphthalimide and acetonitrile. *N*-Vinylphthalimide is probably formed from the azirine by rearrangement of an intermediate carbene (Scheme 2). The fragmentation of azirines in this way, to give carbenes and nitriles, could account for the products of some other reactions,[3] and may be a more general reaction of azirines than has hitherto been recognised.†



SCHEME 2

The diphenyltriazole (**1b**), when pyrolysed in the same way, gave two products: 2,3-diphenyl-2-phthalimido-2*H*-azirine (**2b**), m.p. 180°, and 2-phenyl-3-phthalimidoindole, m.p. 209—211°. The indole was identified by comparison with an authentic specimen, prepared by condensation of 3-amino-2-phenylindole[4] with phthalic anhydride. Again, the indole was shown to be a secondary product, in this case derived by rearrangement of the azirine (**2b**). This type of rearrangement has been observed with other 2-aryl-2*H*-azirines.[3b,5] By varying the pyrolysis temperature, the triazole could be directed to give exclusively the azirine (**2b**) (at 425°) or exclusively the indole (at 500°).

The conversion of these triazoles into 2*H*-azirines is thought to involve the formation and rearrangement of 1*H*-azirines.[6]

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† Another example is the fragmentation of 2,3-diethyl-2-phthalimido-2*H*-azirine; this azirine gives a high yield of *cis*- and *trans*-*N*-prop-1-enylphthalimide when pyrolysed at 500°.

[1] D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Comm.*, 1969, 147.

[2] H. von Pechmann and W. Bauer, *Ber.*, 1909, **42**, 665; R. Stolle, W. Munch, and W. Kind, *J. prakt. Chem.*, 1904, **70**, 433.

[3] (a) W. Bauer and K. Hafner, *Angew. Chem. Internat. Edn.*, 1969, **8**, 772; (b) J. H. Bowie and B. Nussey, *Chem. Comm.*, 1970, 1565.

[4] F. Angelico and S. Capuano, *Gazzetta*, 1937, **67**, 633.

[5] K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Letters*, 1968, 3499; H. Hemetsberger, D. Knittel, and H. Weidmann, *Monatsh.*, 1970, **101**, 161; T. L. Gilchrist, C. W. Rees, and E. Stanton, *J. Chem. Soc.* (*C*), 1971, 3036.

[6] T. L. Gilchrist, G. E. Gymer, and C. W. Rees, following communication.