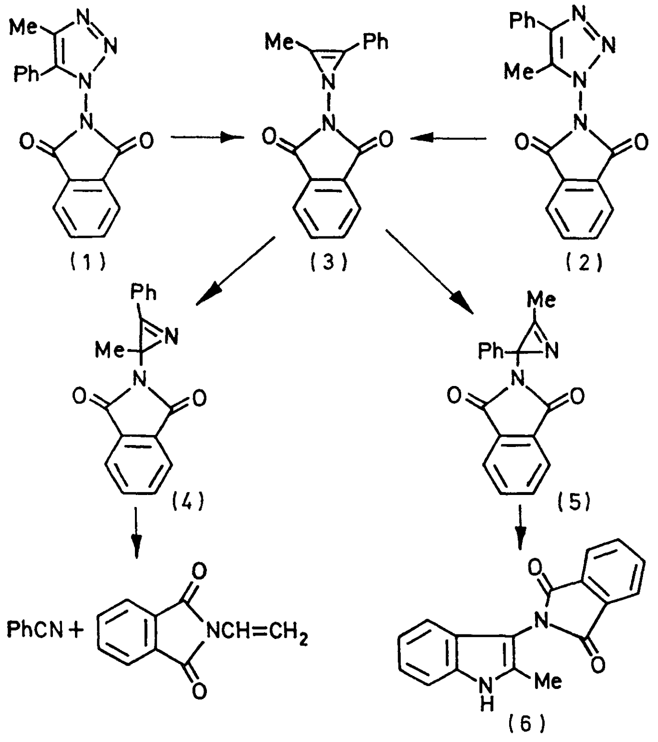
Mechanism of the Pyrolysis of 1,2,3-Triazoles. 1*H*-Azirines as Intermediates

By T. L. GILCHRIST, G. E. GYMER, and C. W. REES*

(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

Summary The isomeric triazoles 4-methyl-5-phenyl-1-phthalimido-1,2,3-triazole (**1**) and 5-methyl-4-phenyl-1-phthalimido-1,2,3-triazole (**2**) have been pyrolysed in the vapour phase at 400—500°, and give the same products, which involve the antiaromatic 1*H*-azirine derivative, 2-methyl-3-phenyl-1-phthalimido-1*H*-azirine (**3**), as a common intermediate.

THE demonstration[1] that 2*H*-azirines are formed in the pyrolysis of 1-phthalimido-1,2,3-triazoles raises the question of the intermediacy of 1*H*-azirines in the reaction. Antiaromatic 1*H*-azirines have been suggested as highly reactive intermediates in the cycloaddition of *N*-phthalimidonitrene to alkynes,[2] where 2*H*-azirines are also the products isolated, and a similar rearrangement could account for the formation of 2*H*-azirines in the triazole pyrolyses.



In order to investigate this possibility, the isomeric triazoles 4-methyl-5-phenyl-1-phthalimido-1,2,3-triazole (**1**), m.p. 180—181°, and 5-methyl-4-phenyl-1-phthalimido-1,2,3-triazole (**2**), m.p. 215—216°, were synthesised: the intermediacy of a 1*H*-azirine derivative (**3**) in the pyrolyses should lead to the formation of identical products from the two triazoles. The synthesis involved the cyclisation of the bis-*p*-toluenesulphonylhydrazone of 1-phenylpropane-1,2-dione with KOH in ethylene glycol, which gave a 3:1 mixture of two 1-*p*-toluenesulphonylamido-1,2,3-triazoles. These were separated by chromatography and hydrolysed to the corresponding 1-aminotriazoles. The minor isomer was assigned the structure 1-amino-4-methyl-5-phenyl-1,2,3-triazole, and the major isomer the structure 1-amino-5-methyl-4-phenyl-1,2,3-triazole, on the basis of their n.m.r. spectra: the phenyl protons of the 5-phenyl derivative appear as a singlet, and those of the 4-phenyl derivative as a multiplet.[3] Condensation with phthalic anhydride then gave the 1-phthalimido-derivatives (**1**) and (**2**).

Pyrolysis of the triazoles at 400—500° and 0·02 mmHg gave the same five products from both, and in the same proportions, as estimated from the n.m.r. spectra of the total products. These products were 2-methyl-3-phenyl-2-phthalimido-2*H*-azirine (**4**), 3-methyl-2-phenyl-2-phthalimido-2*H*-azirine (**5**), 2-methyl-3-phthalimidoindole (**6**), *N*-vinylphthalimide, and benzonitrile. Authentic specimens of the azirines (**4**), m.p. 139—140°, and (**5**), m.p. 119—120°, and of the indole (**6**), m.p. 225—226°, were synthesised for comparison. The methyl groups of the azirines (**4**) and (**5**) appeared in the 100 MHz n.m.r. spectra as singlets at τ 8·13 and 7·30, respectively, and that of the indole (**6**), at τ 7·78. The clear separations of these signals, which were also distinct from those of the methyl groups of the triazoles (**1**) and (**2**) (τ 7·56 and 7·62, respectively) enabled the products to be estimated from the n.m.r. spectra. Preparative layer chromatography of the reaction mixtures then gave pure specimens of the azirine (**4**), *N*-vinylphthalimide, and the indole (**6**); the azirine (**5**) was also isolated but could not be completely separated from its isomer (**4**).

As in the triazole pyrolyses described earlier,[1] it was demonstrated that the indole (**6**) and *N*-vinylphthalimide were secondary products, derived from the azirines (**5**) and (**4**), respectively. Pyrolysis of the azirine (**4**) at 500° gave *N*-vinylphthalimide and benzonitrile, but not indole (**6**); pyrolysis of the azirine (**5**) gave the indole, but no *N*-vinylphthalimide. This rules out a thermal equilibration of the azirines (**4**) and (**5**) as a source of the product mixtures. A ready equilibration of this type has been observed with chloro-azirines,[4] but evidently does not occur with phthalimido-azirines. Thus, equilibration must occur before formation of the 2*H*-azirines; the 1*H*-azirine (**3**) is therefore implicated as a common intermediate. The partial recovery of the triazole (**1**) after pyrolysis at 440°, and the failure to detect any of this triazole in the pyrolysis products of triazole (**2**) at 400°, rules out any equilibration of the starting triazoles.

The similarity of the product ratios from the two triazoles suggests that the reactions proceed almost entirely through the antiaromatic intermediate (**3**). This conclusion is in contrast to that of other investigators who have attempted to detect 1*H*-azirine intermediates in triazole decompositions,[5] and it remains to be established what the precise requirements are for the 1*H*-azirine mechanism to be favoured.

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