Hydrogen Transfer in Iminocarbenes; a New Synthesis of Isoquinolines

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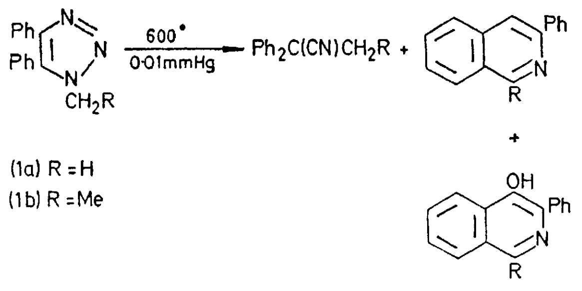
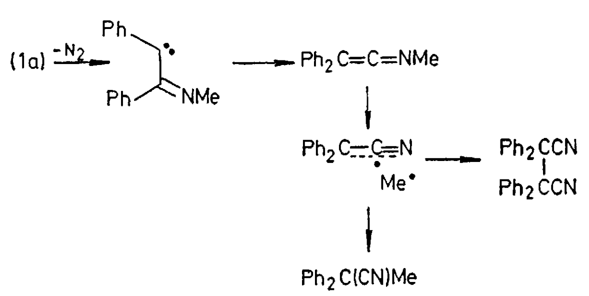
Summary When 1-alkyl-4,5-diphenyltriazoles are pyrolysed in the vapour phase nitrogen is extruded and the remaining iminocarbene reacts both by Wolff rearrangement, and by what is considered to be a new 1,4-hydrogen transfer from the alkyl group leading to 3-phenylisoquinolines.

THE chemistry of α-ketocarbenes has been studied extensively, but much less is known of the reactions of the corresponding iminocarbenes. Although the chemistry of the two types of intermediate should be broadly similar, the presence of an additional substituent on the nitrogen atom of iminocarbenes extends the possible range of reactions. The pyrolytic extrusion of nitrogen from 1*H*-1,2,3-triazoles represents a suitable method for the generation of iminocarbenes.[1]

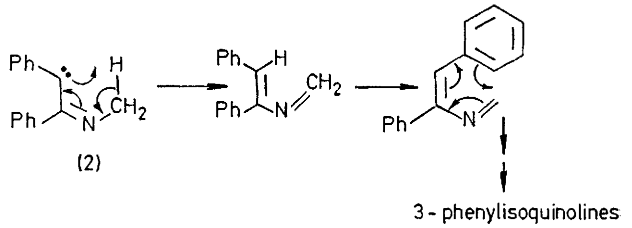
1-Methyl-4,5-diphenyl-1,2,3-triazole (**1a**), m.p. 129—130°, and 1-ethyl-4,5-diphenyl-1,2,3-triazole (**1b**), m.p. 110—111°, were prepared by alkylation of the silver salt of 4,5-diphenyl-*v*-triazole with iodomethane and iodoethane, respectively. Pyrolysis[2] of (**1a**) at 600° and 0·01 mmHg gave three major products (Scheme 1) identified by comparison with independently prepared specimens: 2,2-diphenylpropionitrile (51%),† 3-phenylisoquinoline (19%), and 4-hydroxy-3-phenylisoquinoline (12%).‡ 2,2-Diphenylpropionitrile is probably formed from diphenylketen *N*-methylimine, the product to be expected from Wolff rearrangement of the carbene (Scheme 2); an independently prepared specimen of the ketenimine gave 2,2-diphenylpropionitrile (63%) when pyrolysed at 600°. Another product (21%) of the ketenimine pyrolysis is tetraphenylsuccinodinitrile, which was also detected as a minor product of the triazole pyrolysis. The formation of this compound, the dimer of a highly stabilised radical, indicates that this new ketenimine rearrangement probably proceeds by a radical mechanism. The formation of isoquinolines is considered to be most simply explained by a new type of carbene reaction, a 1,4-hydrogen transfer from the *N*-methyl group, followed by *cis–trans* isomerisation, electrocyclic ring closure, and oxidation (Scheme 3). This hydrogen transfer may be a [1,4] sigmatropic shift in the singlet carbene (**2**) or could involve intramolecular abstraction by the triplet carbene. 4-Hydroxy-3-methylisoquinoline is presumably formed by peroxidation and dehydration of an intermediate dihydroquinoline.



SCHEME 1

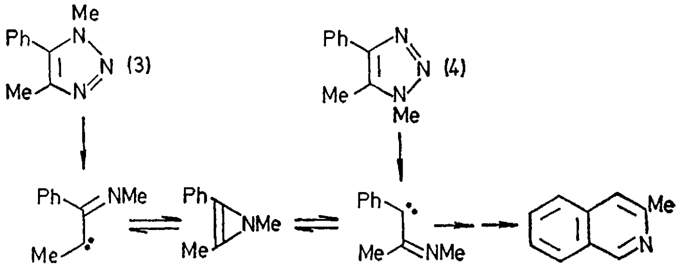


SCHEME 2



SCHEME 3

Analogous reactions were observed with (**1b**), the products being 2,2-diphenylbutyronitrile (44%), 1-methyl-3-phenylisoquinoline (6%), and 4-hydroxy-1-methyl-3-phenylisoquinoline (13%).



SCHEME 4

In earlier work it was shown that the pyrolysis of 1-phthalimido-1,2,3-triazoles involves a transient symmetrical intermediate, for which a 1*H*-azirine structure was sug-

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† All yields are for isolated compounds.

‡ This yellow compound, m.p. 160·5—161·5°, not hitherto reported, was prepared by the reaction of acetic anhydride with 3-phenylisoquinoline *N*-oxide, using a procedure analogous to that for the preparation of 4-hydroxy-3-methylisoquinoline (M. M. Robison and B. L. Robison, *J. Org. Chem.*, 1956, **21**, 1337).

gested.[1] The 1-alkyltriazoles also give a symmetrical intermediate on pyrolysis, since both 1,4-dimethyl-5-phenyltriazole (**3**) and 1,5-dimethyl-4-phenyltriazole (**4**) gave 3-methylisoquinoline as a product. The carbenes derived from these triazoles may be interconverted *via* a symmetrical 1*H*-azirine intermediate (Scheme 4) before the irreversible conversion of one of these carbenes into 3-methylisoquinoline.

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[1] T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1973, 555.

[2] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.