1,4-Hydrogen Transfer in the Thermal Decomposition of But-3-enyl-2*H*-azirines

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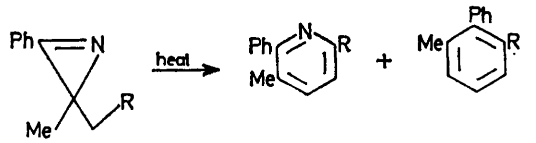
Summary Thermolysis of but-3-enyl substituted 2*H*-azirines gives substituted pyridines and biphenyl derivatives *via* 1,4-hydrogen transfer from the methylene group of an intermediate vinylnitrene.

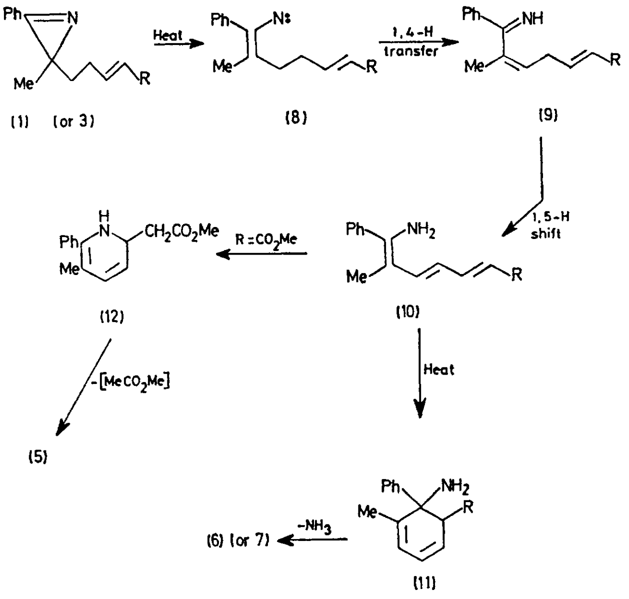
THE products formed on thermal decomposition of 2*H*-azirines generally appear to involve C–N rather than C–C bond cleavage.[1,2] In some cases, C–N bond cleavage ultimately leads to fragmentation of the three-membered ring with the subsequent formation of a nitrile and carbene[1a,b] and in other cases results in the formation of indoles[1a,d] or pyrroles.[1e] Here we describe a previously unobserved thermal reaction in the 2*H*-azirine system, and call attention to a novel 1,4-hydrogen transfer which occurs from an intermediate vinylnitrene.



(1) R = $CH_2CH{=}CH_2$ (4) R = Me   (6) R = H
(2) R = CH_2CHO (5) R = H   (7) R = CO_2Me
(3) R = $CH_2CH{=}CHCO_2Me$

The azirine (**1**) was prepared by a modified Neber reaction in which 2-methyl-1-phenylhex-5-en-1-one was treated with dimethyl hydrazine followed by MeI and base. When a solution of (**1**) in toluene was heated at 195 °C for several days, two products were isolated in good overall yield. The major product (49%) was identified as 2-methylbiphenyl (**6**) while the minor product (15%) was assigned as 2,5-dimethyl-6-phenylpyridine (**4**); in each case the material isolated was compared with an authentic specimen.[3]

We then studied the thermal behaviour of the related azirines (**2**) and (**3**), which were readily prepared by ozonisation of (**1**) followed by reaction of the 2*H*-azirine aldehyde (**2**) with $MeO_2CCH{=}PPh_3$. The only product obtained (55% isolated yield) from the thermolysis of (**2**) was 2-phenyl-3-methylpyridine (**5**), which was identified by comparison with an authentic sample.[4] When the azirine (**3**) was heated for several days in a toluene solution at 195 °C, it produced 2-phenyl-3-methylpyridine (**5**) (58%) as well as methyl 6-methylbiphenyl-2-carboxylate (**7**) (12%). The structure of this ester was verified by hydrolysis to the known 6-methylbiphenyl-2-carboxylic acid.[5]



SCHEME

The formation of the substituted biphenyl derivatives (**6** and/or **7**) can be explained by the sequence shown in the Scheme. Thermal equilibration of the 2*H*-azirine with a transient vinylnitrene (**8**)[6] followed by a 1,4-hydrogen transfer from the methylene group generates the azatriene (**9**), which undergoes a thermally allowed 1,5-sigmatropic hydrogen shift to give the triene (**10**). Electrocyclic closure of (**10**) to the cyclohexadiene (**11**) followed by loss of ammonia accounts for the formation of the substituted biphenyl derivatives. The isolation of (**5**) can also be accounted for by an internal Michael addition of (**10**) to

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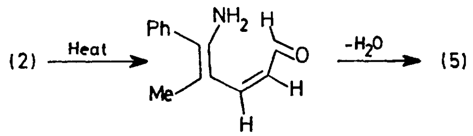
† All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given later.



(13)

give (**12**) followed by loss of methyl acetate. The key feature of this mechanism is the 1,4-hydrogen transfer. Related hydrogen transfers have been observed in reactions of vinylcarbenes[7] and more recently with iminocarbenes.[8] The proposed 1,4-hydrogen transfer was further substantiated by the thermal conversion of (**2**) into (**5**). In this case, a series of 1,4 and 1,5 hydrogen transfers give (**13**) which can only cyclise to (**5**).

The formation of small quantities of (**4**) from the thermolysis of (**1**) is also of interest. It could be formed by a competitive intramolecular addition of the vinylnitrene on to the adjacent π-bond to give a bicycloaziridine which forms the observed product by ring opening followed by oxidation.

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[1] (a) D. J. Anderson, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1973, 550; (b) T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *ibid.*, p. 555; (c) K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Letters*, 1968, 3499; (d) K. Isomura, M. Okada, and H. Taniguchi; *ibid.*, 1969, 4073; (e) *Chem. Letters*, 1972, 629; (f) T. Nishiwaki, *J.C.S. Chem. Comm.*, 1972, 565; R. Selvarajan and J. H. Boyer, *J. Heterocyclic Chem.*, 1972, **9**, 87; T. Nishiwaki, A. Nakano, and H. Matsuoka, *J. Chem. Soc.* (*C*), 1970, 1825; J. H. Bowie and B. Nussey, *Chem. Comm.*, 1970, 1565; D. Knittel, H. Hemetsberger, R. Leipert, and H. Weidemann, *Tetrahedron Letters*, 1970, 1459; N. S. Narashimhan, H. Heimgartner, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 1351.

[2] For a recent example where C–C bond cleavage of a 2*H*-azirine occurs thermally see L. A. Wendling and R. G. Bergman, *J. Amer. Chem. Soc.*, 1974, **96**, 308; A. Demoulin, H. Gorissen, A. M. H. Frisque, and L. Ghosez, *ibid.*, 1975, **97**, 4409.

[3] J. M. Bonnier and J. Court, *Bull. Soc. chim. France*, 1970, 142.

[4] R. A. Ambramovitch, G. S. Seng, and A. D. Notation, *Canad. J. Chem.*, 1960, **38**, 761.

[5] R. D. Howorth and P. B. Tinker, *J. Chem. Soc.*, 1955, 911.

[6] T. Nishiwaki and F. Fujiyama, *J.C.S. Perkin I*, 1972, 1456.

[7] E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergmann, *J. Amer. Chem. Soc.*, 1973, 95, 5680; J. A. Pinock, R. Morchat, and D. R. Arnold, *ibid.*, p. 7536; G. L. Closs, L. E. Closs, and W. A. Boll, *ibid.*, 1963, **85**, 3796; R. Srinivasan, *ibid.*, 1969, **91**, 6250; *Chem. Comm.*, 1971, 1041; R. D. Streeper and P. D. Gardner, *Tetrahedron Letters*, 1973, 767.

[8] T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1975, 1.