

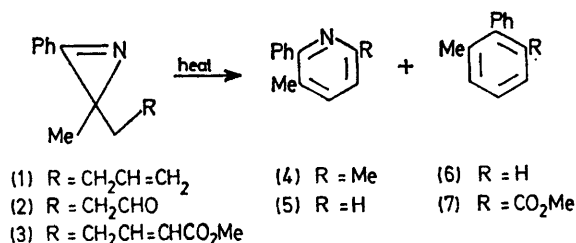
1,4-Hydrogen Transfer in the Thermal Decomposition of But-3-enyl-2*H*-azirines

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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.

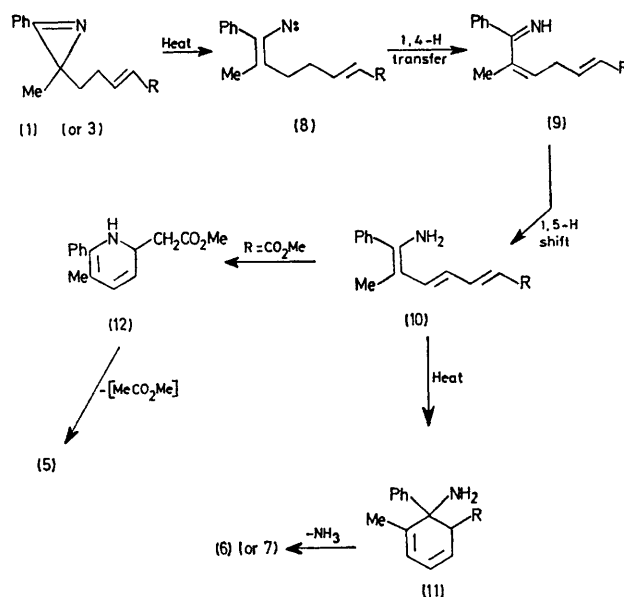
THE products formed on thermal decomposition of 2*H*-azirines generally appear to involve C-N rather than C-C bond cleavage.^{1,2} In some cases, C-N bond cleavage ultimately leads to fragmentation of the three-membered ring with the subsequent formation of a nitrile and carbene^{1a,b} and in other cases 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.



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 $\text{MeO}_2\text{CCH}=\text{PPh}_3$. 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

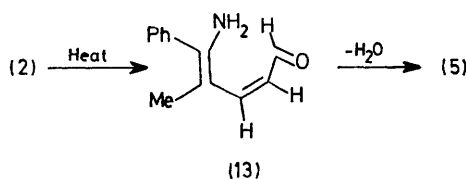
(3) was heated for several days in a toluene solution at 195 °C, it produced 2-phenyl-3-methylpyridine (5) (58%) as well as methyl 6-methylbiphenyl-2-carboxylate (7) (12%). The structure of this ester was verified by hydrolysis to the known 6-methylbiphenyl-2-carboxylic acid.⁵



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

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



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 vinylcarbenes⁷ and more recently with iminocarbenes.⁸ The proposed 1,4-hydrogen transfer was further substan-

tiated 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.

We thank the National Institutes of Health for financial support.

(Received, 4th August 1975; Com. 892.)

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