Stereoselectivity in Addition of *N*-nitrenes to Dienes

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Summary Addition of *N*-nitrenes, derived from (**1**) and (**6**), to various dienes at low temperature, gives vinylaziridines with heterocycle and vinyl group in preferential *syn* orientation.

OXIDATION of 3-aminobenzoxazol-2(3*H*)-one (**1**) with lead tetra-acetate in the presence of isoprene is known to give the aziridines (**2a**), (**2b**), and (**3b**).[1] A 61 : 39 ratio of (**2a**) : (**2b**) is observable by n.m.r. as a result of slow inversion at the aziridine ring nitrogen. The presence of signals from only (**3b**) in the n.m.r. spectrum of this aziridine is attributable to the greater thermodynamic stability of this invertomer relative to (**3a**).

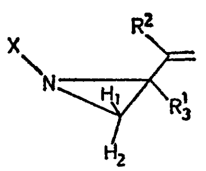
We have repeated the oxidation of (**1**) with lead tetra-acetate in the presence of isoprene at −30 °C in $CDCl_3$ and have examined the total reaction mixture at this temperature without allowing any intermediate warming of the solution. Under these conditions only (**2a**), (**2b**), and (**3a**) are present (ratio 43 : 15 : 42); we note that (**3b**) is completely absent. If the solution is warmed to 0 °C the gradual appearance of signals from (**3b**) is observed with a corresponding loss in intensity of those from (**3a**). Assignments of the aziridine ring protons are summarised in the Table. First-order conversion of (**3a**) into (**3b**) ($t_{\frac{1}{2}}$ *ca.* 20 min at 5 °C) is complete before thermodynamic equilibration of (**2a**) and (**2b**) ($t_{\frac{1}{2}}$ *ca.* 5×10^3 min at 5 °C) is appreciable. Thus the observed ratio of (**2a**) : (**2b**) at −30 °C is a true kinetic ratio in which no adventitious equilibration has occurred. At room temperature, the ratio of (**2a**) : (**2b**) : (**3b**) shown by n.m.r. is 35 : 23 : 42 and is unchanged on re-cooling to −30 °C, and (**3a**) is not visible.

Surprisingly therefore, although addition to the disubstituted double bond of isoprene is only moderately stereoselective, addition to the monosubstituted double bond gives only the thermodynamically less stable invertomer (**3a**). A consistent pattern emerges when the oxidative addition of (**1**) to butadiene and 2,3-dimethylbutadiene is examined at −30 °C. Using butadiene, addition occurs exclusively *syn* to the vinyl group to give (**4a**). After thermodynamic equilibration, complete conversion into the *anti*-isomer (**4b**) is observed (Table). Addition to 2,3-dimethylbutadiene results in a 75 : 25 kinetic ratio of (**5a**) : (**5b**) at −30 °C with a thermodynamic equilibrium ratio of 15 : 85.

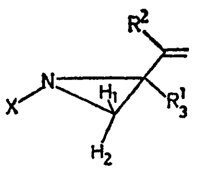
TABLE

Compound		Chemical shift δ			Coupling constant/Hz		
		H_1	H_2	$H_3(R_3^1)$	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
(**2a**)	R^1 = Me, R^2 = H	3·38d	2·61d	—	3·0	—	—
(**2b**)	R^1 = Me, R^2 = H	2·56d	3·38d	..	3·0	—	—
(**3a**)	R^1 = H, R^2 = Me	3·78dd	2·64dd	3·01t	3·5	6·2	6·2
(**3b**)	R^1 = H, R^2 = Me	2·56dd	2·90dd	3·12dd	2·0	5·2	7·5
(**4a**)	R^1 = H, R^2 = H	3·28dd	2·73dd	3·08q	2·8	5·9	6·3
(**4b**)	R^1 = H, R^2 = H	2·47m	3·05m	3·05m	(second order spectrum)		
(**5a**)	R^1 = Me, R^2 = Me	4·24d	2·33d	—	3·5	—	—
(**5b**)	R^1 = Me, R^2 = Me	2·58d	3·22d	—	2·5	—	—

Spectra measured in $CDCl_3$–Me_4Si at −30 °C. Possible small changes in chemical shift due to variations in concentration have not been investigated.

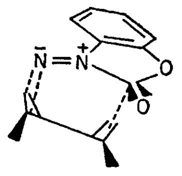


(2a)

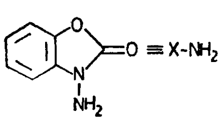


(2b)

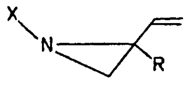
Substitution of *N*-aminophthalimide (**6**) for (**1**) in the above reaction gives very similar results. The only other reported examples of completely stereoselective nitrene additions to olefins are the oxidative addition of (**6**) to methyl acrylate and methyl methacrylate, in which the phthalimide and ester groups are placed *syn* in the initially formed aziridines.[2] Our observation of this selectivity, not only in addition to dienes, but also to styrene, and α- and β-methyl-styrene,[3] suggests that the peculiar affinity of these reactive intermediates for π-electron-containing substituents on olefins is a general phenomenon. The stereoselectivities reported here are far higher than those found for addition of free carbenes[4] and are the result, we believe, of a strong attractive interaction (Figure) between the substituent on the olefin and the highly electrophilic amide carbonyl carbon in the nitrene.[5] As a consequence of such interaction any nucleophilic[6] character of the nitrene is assisted by electron back-donation from a substituent on the receptor olefin. A requirement for the *s-cis*-conformation of the diene is implicit in the Figure. Low-temperature addition of the nitrene derived from (**6**) to 2,5-dimethylhexa-2,4-diene gave a 12:88 ratio of (**7a**):(**7b**) in lower yield. Using 4-methylpenta-1,3-diene, no aziridine could be detected even with excess of olefin. The reluctance of these two dienes to assume *s-cis*-conformations may be responsible both for the lower yields of aziridines and the absence of *syn*-selectivity.



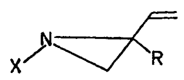
FIGURE



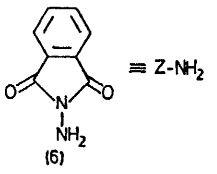
(1)



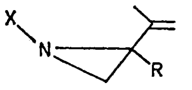
(2a) R = Me
(4a) R = H



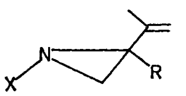
(2b) R = Me
(4b) R = H



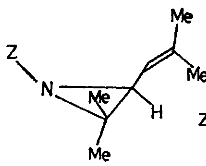
(6)



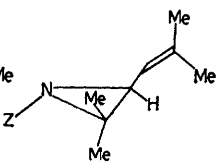
(3a) R = H
(5a) R = Me



(3b) R = H
(5b) R = Me



(7a)



(7b)

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