Intramolecular Addition of *N*-Nitrenes to Alkenes: Transition from Non-concerted to Concerted Addition

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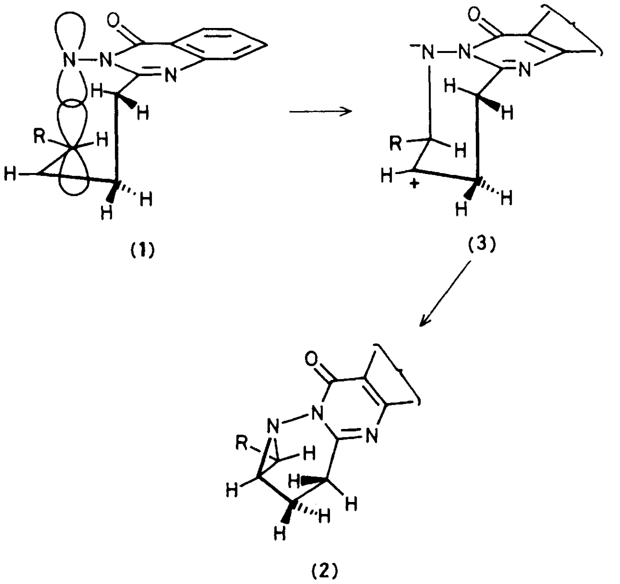
The nitrenes generated by oxidation of the *N*-amino compounds (**6**) and (**7**) are trapped competitively by the phenyl-substituted and unsubstituted double bonds: the grossly different selectivity of the nitrenes for the two double bonds in each case has been interpreted in terms of a change in mechanism from non-concerted to concerted and has allowed a description of the likely transition state geometry in the latter case.

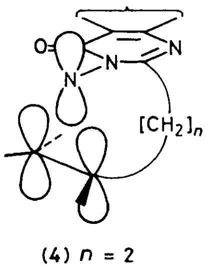
Intramolecular addition of the quinazolone *N*-nitrene to the alkene in (**1**) giving aziridine (**2**) has been interpreted as proceeding *via* an intermediate having high dipolar character (**3**),[1] Scheme 1. The non-concertedness of this addition was rationalised by assuming that the sp-hybridised nitrene attacks the double bond as indicated in (**1**) with overlap of the empty p-orbital of the nitrene with the terminal p-orbital of the double bond. The tight belt of atoms connecting nitrene and alkene even in (**1**) made the further deformation required for overlap as in (**4**) seem unlikely.



R = Ph, H
Scheme 1

We now present evidence that extension of this belt of atoms in (**1**) by one carbon atom brings about a change in mechanism for attack of the nitrene on the alkene to one with a transition state resembling (**5**).

Whereas oxidation of (**6**) results in little selectivity of the derived nitrene for the phenyl-substituted *vs.* unsubstituted double bonds (ratio 1.5 : 1,† respectively), the corresponding selectivity of the nitrene derived from oxidation of (**7**) is high (ratio 8.5 : 1, respectively). This change in ratio signals either a change in mechanism of nitrene addition, or conceivably,



(**4**) n = 2
(**5**) n = 3

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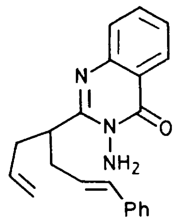
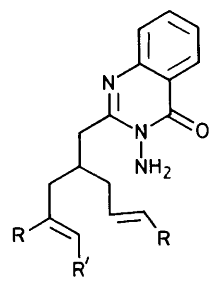
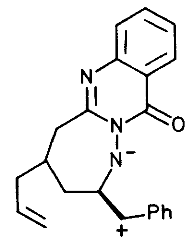
† This value was earlier given as *ca.* 1 : 1 from examination of the 90 MHz spectrum of the crude product (ref. 1): re-measurement at 400 MHz gives this revised ratio.

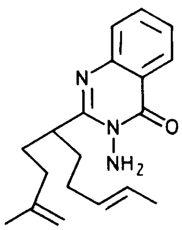
competitive attack on the β-carbon atom of the phenyl-substituted double bond and on the α-carbon atom of the unsubstituted double bond with intermediates having high dipolar character being generated in each case: preferential attack on the phenyl-substituted double bond would then be attributable to benzylic stabilisation of the carbonium ion in the intermediate (**8**).

Attack of the nitrene generated by oxidation of (**9**) takes place on both α-methyl- and β-methyl-substituted double bonds with almost equal facility (ratio 1 : 1.05, respectively) but we recognise that this ratio does not reflect the real relative affinities of these double bonds for the nitrene since the corresponding ratio in oxidation of the α-branched analogue (**10**) is 1 : 3. Addition to one face of the β-methyl-substituted double bond in (**9**) is inhibited by adverse steric interaction (see below) and the reaction is stereoselective giving mostly (**11**) (Scheme 2). In contrast, addition of the nitrene to the α-methyl-substituted double bond in (**9**) and to the two double bonds in (**7**) is non-stereospecific with both faces of the double bonds being attacked in each case: *the ratio of stereoisomers produced in all three cases is the same* (Scheme 2).


(6)


(7) R = H, R′ = Ph
(9) R = Me, R′ = H

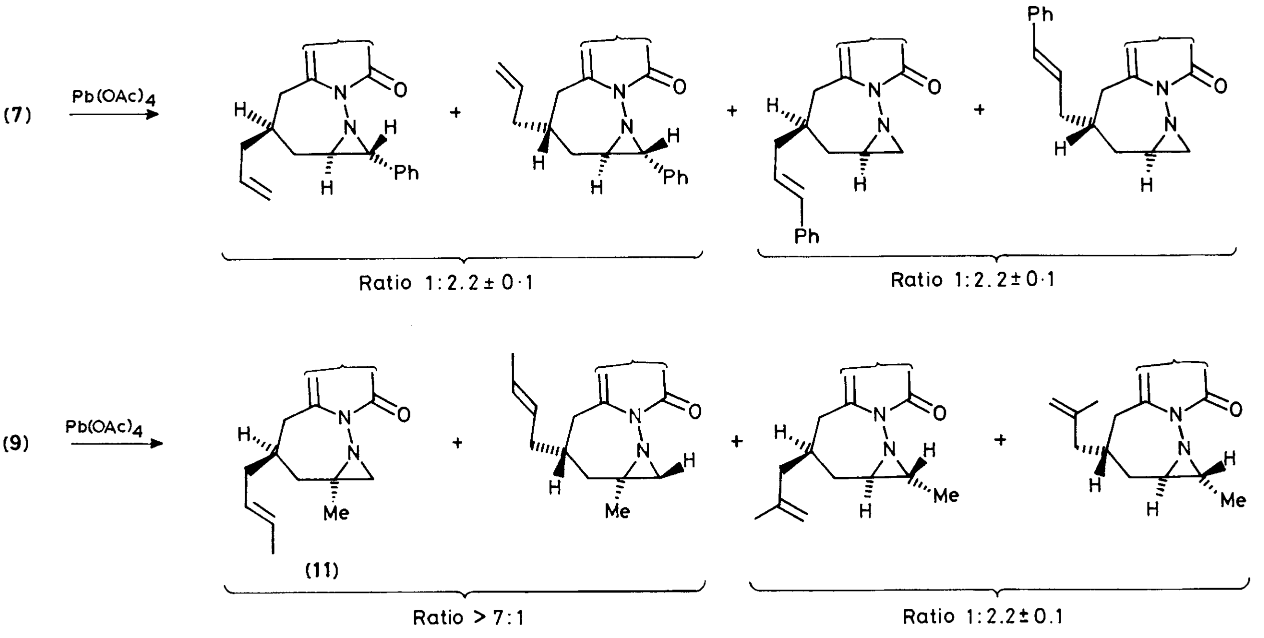

(8)


(10)

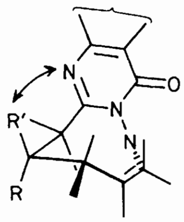
We arrive at this conclusion from examination of the 400 MHz spectra on the crude oxidation products of (**7**) and (**9**). Interpretation of these spectra is facilitated by the quantitative yields (n.m.r.) of aziridines obtained and by the single conformation of the seven-membered ring in each case with the result that the configurations of the alkenylmethyl side chains are definable from analysis of coupling constants. Confirmation of assignments was made by comparison of these spectra of the crude products with those of the separated isomers and, in some cases, stereoisomers.

Although the additional carbon in the side chains of (**7**) and (**9**) allows some increased flexibility in attack of the nitrene on either double bond [by comparison with (**6**)], an examination of Dreiding models suggests that the chain is still sufficiently tight for identifiably different conformations to be necessary for attack on the α- and β-carbon atoms of the alkenes. Representations of these two conformations are shown in structures (A) and (B), respectively, with the significant differences in eclipsing or steric strain elements shown by arrows.

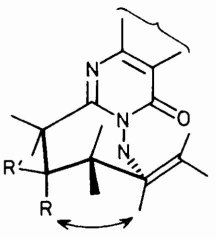
We believe that a switch from attack on the α- to the β-position would, as a result of those conformational differences between (A) and (B), be accompanied by a significant change in stereoisomer ratio: specifically, reaction *via* (B) would be expected to result in more of the stereoisomer with R=H. Identical stereoisomer ratios, however, would be anticipated if attack of the nitrene on both double bonds in (**7**) and on the α-methyl-substituted double bond in (**9**) was intermediate between (A) and (B) [*cf.* (**5**)]. This proposed transition state leads directly to what our n.m.r. interpretation



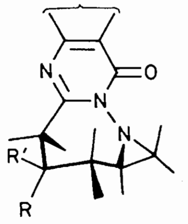
Scheme 2



(A)



(B)



(C)

R, R' = H, alkenylmethyl (phenyl-, α- and β-methyl- and unsubstituted) side chain.

shows is the only conformation (C) present in the aziridines in Scheme 2. It is clear also why attack on one face of the double bond bearing a β-methyl is particularly favoured since attack on the other face would involve methyl–CH_2 (alkenyl) repulsion.

A change in mechanism is, therefore, implicated in the nitrene additions to double bonds in (**7**) and (**9**) by comparison with those in (**6**). The greater reactivity of the phenyl-substituted double bond in (**7**) over the unsubstituted double bond *via* a transition state (**5**) can be ascribed to better HOMO (alkene)–LUMO (nitrene) overlap in the former case *i.e.* the change in mechanism referred to above is a change from non-concerted to concerted addition.

We thank the S.E.R.C. for financial support, the University of Warwick high-field n.m.r. service for spectra, and Antoinette Bathgate for experimental assistance.

Received, 13th May 1985; Com. 658

Reference

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