Stereospecific Addition of an Amino-nitrene to Mono- and Di-enes

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IN contrast with carbenes, few examples of the trapping of nitrenes with olefins to form aziridines have been reported. Apart from the extensive work of Lwowski and colleagues with ethoxycarbonylnitrene,[1] the addition of ethoxycarbonylnitrene to buta-1,3-diene and of methoxycarbonylnitrene to *cis*- and *trans*-but-2-ene,[2] of cyanonitrene to cyclo-octatetraene,[3] and of nitrene to ethylene[4] and to buta-1,3-diene[5] has been recorded. We now describe the stereospecific synthesis of aziridines by the addition of an amino-nitrene† to mono- and di-enes.

Amination of benzoxazolin-2-one with hydroxylamine-*O*-sulphonic acid readily gave 3-aminobenzoxazolin-2-one (I),‡ m.p. 169—170°, λ_{max} 229 mμ (ϵ 9240), 275 (5020), (benzylidene derivative, m.p. 158—159°, butylidene derivative, m.p. 55—57°), whose structure was confirmed by reconversion into benzoxazolinone with *N*-nitrosodiphenylamine. By analogy with 1-aminobenzotriazole,[6] oxidation of (I) with lead tetra-acetate should give the nitrene (II) which, formally, could fragment to benzyne, carbon dioxide, and nitrogen.

Although (I) was rapidly oxidised with lead tetra-acetate in methylene chloride at or below room temperature this fragmentation was not observed; added tetracyclone was rapidly decolourised, but gave a yellow 1 : 1-nitrene adduct rather than tertaphenylnaphthalene (*cf.*, ref. 6). Oxidation in the presence of a large excess of *cis*- and of *trans*-but-2-ene in methylene chloride gave respectively the *cis*-adduct (III) (60%), m.p. 88—89°, λ_{max} 236 mμ (ϵ 9100), 277 (5320), and the *trans*-adduct (IV) (67%), m.p. 65—65·5°, λ_{max} 237 mμ (ϵ 8620), 278 (5070), stereospecifically.§ None of the other isomer was detected in each case, even with only 1·5 moles of olefin at 2 mole % concentration in methylene chloride. At this dilution, McConaghy and Lwowski[1] observed substantial non-stereospecific addition of ethoxycarbonylnitrene as a result of singlet to triplet decay. Since 5% of (III) or (IV) was readily detected in the other, the stereospecificity was greater than 95%, the highest yet observed for a

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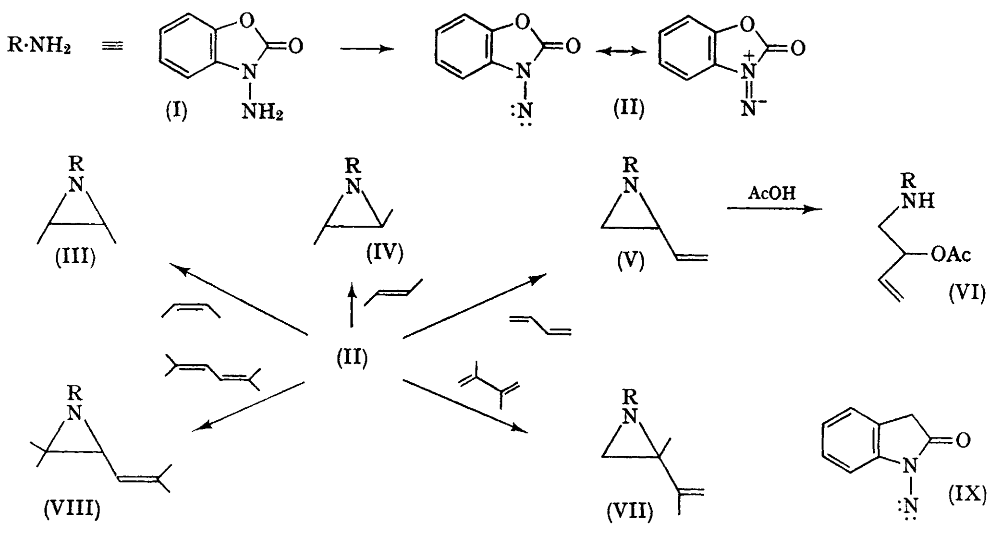
† The species $R_2N{-}N{:}\longleftrightarrow R_2N^+{=}N^-$ have been variously named as azamines, azaimines, diazenes, diazines, and amino-imido-intermediates; although their fragmentation reactions have been widely investigated, their reaction with olefins has not previously been reported (R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 174).

‡ Satisfactory microanalytical and infrared data were obtained for all new compounds reported in this and the following Communication.

§ The n.m.r. spectra of the aziridinobenzoxazolinones are complicated by the existence of single invertomers, on the n.m.r. time-scale, and by deshielding by the benzoxazolinone substituent of the aziridine ring protons *cis* to it.

nitrene addition. Thus it appears that the aminonitrene is generated and trapped in the singlet state (II), which is highly stabilised by the delocalisation shown and is probably the ground state.



Oxidation of (I) in the presence of conjugated dienes led to exclusive 1,2-addition, and none of the pyrrolines[7] which would result from 1,4-addition were detected. Thus buta-1,3-diene gave 3-(2-vinylaziridino)benzoxazolinone (V)¶ (71%), m.p. 70·5—71°, whose structure was confirmed by the mass spectrum [*m/e* 202 (M^+), 134 and 68 (N–N bond fission), 135 and 67 (N–N bond fission and hydrogen migration)], by catalytic hydrogenation to 3-butylaminobenzoxazolinone (86%), b.p. 170°/0·5 mm. [identical with the lithium aluminium hydride reduction product of the butylidene derivative of (I)], and by its ready solvolysis in cold acetic acid to give 3-(2-acetoxybut-3-enylamino)-benzoxazolinone (VI) (53%), m.p. 80·5—82°, which on catalytic hydrogenation gave 3-butylamino-(41%) and 3-(2-acetoxybutylamino)benzoxazolinone, m.p. 76·5—78° (53%). 2,3-Dimethylbuta-1,3-diene and 2,5-dimethylhexa-2,4-diene similarly gave the corresponding aziridines (VII) (42%), m.p. 38—38°, and (VIII) (24%), m.p. 92—95°, and isoprene gave a mixture of the two possible aziridines. 1,2-Addition of (II) and of ethoxycarbonylnitrene[2] to buta-1,3-diene contrasts with the claim of 1,4-addition of nitrene itself to butadiene.[5]

No trapping by olefins of the formally similar nitrene (IX), generated by lead tetra-acetate oxidation of *N*-amino-oxindole, was detected in identical conditions. Ring expansion[8] to 3-cinnolinol (60%) supervenes, possibly because of the greater susceptibility of the carbonyl group to intramolecular attack by the nitrene in its dipolar form.

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¶ These vinylaziridines are very sensitive to acid and rapidly decompose on silica; the particularly rapid solvolysis of (VIII) accounts for the low yield of isolated product.

[1] J. S. McConaghy and W. Lwowski, *J. Amer. Chem. Soc.*, 1967, **89**, 2357, 4450.
[2] K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 1964, 3953.
[3] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1965, **87**, 5512.
[4] M. E. Jacox and D. E. Milligan, *J. Amer. Chem. Soc.*, 1963, **85**, 278.
[5] R. Appel and O. Büchner, *Angew. Chem.*, 1962, **74**, 430.
[6] C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 1964, **296**.
[7] R. S. Atkinson and C. W. Rees, following communication.
[8] H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977.