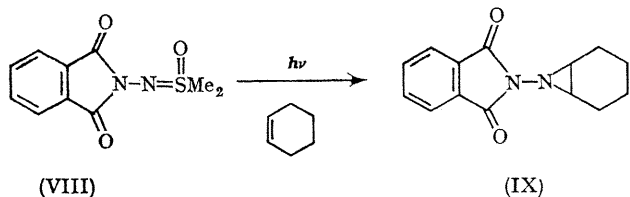
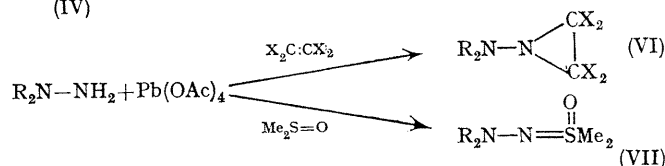
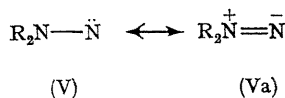
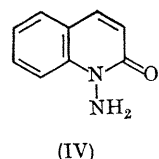
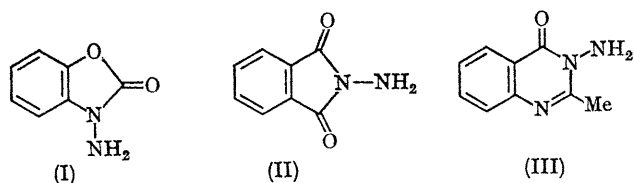


Aziridines from Amines and from Sulphoximines. Nucleophilic Character of Amino-nitrenes

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AZIRIDINES (VI) are formed, stereospecifically and usually in good yield, when the cyclic *N*-amino-compounds, (I—IV), are oxidised by lead tetra-acetate in the presence of olefins



(*cf.* ref. 1). Amino-nitrenes (V) are thought to be intermediates. We report here some further evidence which favours the nitrene mechanism, and some reactions which

indicate that the amino-nitrenes can have nucleophilic character.

We find that acrylic esters and similar olefins in which the double bond is conjugated with an electron-withdrawing group, give good yields of aziridines. Such olefins are usually rather poor traps for carbenes and nitrenes. The carbenes which do add to them readily are thought to have nucleophilic character;² this concept has recently been theoretically justified by Hoffmann.³ It is reasonable to ascribe similar nucleophilic character to amino-nitrenes if the dipolar structure (Va) is an important contributor.

Dimethyl sulphoxide and similar sulphoxides are also effective traps⁴ for these amino-nitrenes, the products of the reactions being the corresponding sulphoximines (VII). A selection of results of these trapping experiments is given in the Table.

TABLE

<i>N</i> -Amino-compound	Olefin	Aziridine (VI) (%) and its m.p.
(I)	Methyl acrylate	96, 83—85°
(II)	Styrene	42, 152°
(II)	Mesityl oxide	88, 67—69°
(II)	Trichloroethylene	90, 96°
(III)	Butadiene	81, 93—95°
(III)	Ethyl methacrylate	62, 107—109°
(III)	<i>cis</i> -Butene	48, 153—154°
(III)	<i>trans</i> -Butene	46, 105—108°
(IV)	Methyl methacrylate	57, 94—97°

<i>N</i> -Amino-compound	Dimethyl sulphoximine (VII) (%) and its m.p.
(I)	60, 164—165°
(II)	75, 208°
(III)	100, 176—178°
(IV)	52, 200—201°

The dimethyl sulphoximines are also precursors of the amino-nitrenes: when they are photolysed in the presence

of olefins, the corresponding aziridines are produced. For example the sulphoximine (VIII) gives the aziridine (IX) (20%, m.p. 137°) when it is photolysed in a mixture of acetonitrile and cyclohexene. The aziridine (IX) is identical to that isolated (40%) from the direct oxidation

of *N*-aminophthalimide in the presence of cyclohexene. The amino-nitrene is the only likely common intermediate in these two reactions.

(Received, December 9th, 1968; Com. 1679.)

¹ R. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1230.

² W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, 1967, **89**, 3069; W. M. Jones, M. E. Stowe, E. E. Wells, and E. W. Lester, *ibid.*, 1968, **90**, 1849; T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Letters*, 1968, 565.

³ R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 5457.

⁴ For other examples of the use of dimethyl sulphoxide as a trap for nitrenes, see L. Horner and A. Christmann, *Chem. Ber.*, 1963, **96**, 388; J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 319; P. Robson and P. R. H. Speakman, *J. Chem. Soc. (B)*, 1968, 463.