Aziridine Dissociation; a Mild Thermal Route to Phthalimidonitrene Adducts

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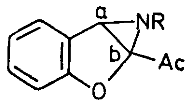
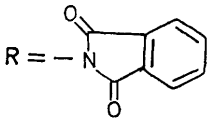
Summary In boiling benzene the aziridine (**1**) transfers phthalimidonitrene to dimethyl sulphoxide, 2-methylfuran, 2-methoxynaphthalene, and a variety of olefins.



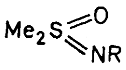
(1)

R = 

throughout

$R-\ddot{N}:$

(2)

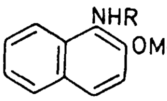


$Me_2S(=O)=NR$

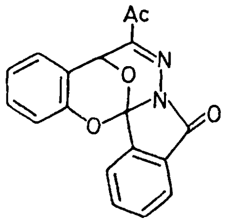
(3)

AcCH=CH·CH=NR

(4)



(5)



(6)

Although the addition of nitrenes to olefins is a familiar reaction, its reversal, the dissociation of an aziridine to a nitrene and an olefin, has only been induced photochemically.[1] We find that in boiling benzene over 5 h the aziridine (**1**) dissociates to 2-acetylbenzofuran and phthalimidonitrene (**2**). Dissociation of (**1**) in the presence of dimethyl sulphoxide gave the sulphoximide (**3**) (41%) whilst with 2-methylfuran the hydrazone (**4**) (30%) was formed; trapping with 2-methoxynaphthalene gave the insertion product (**5**) (34%). The expected aziridines were obtained in the indicated (%) yield in the presence of the following olefins: indene (52), cyclohexene (45), *trans*-stilbene (24), methyl crotonate (32), methyl acrylate (56), mesityl oxide (48), and trichloroethylene (28).†

Evidence favouring the intervention of "free" phthalimidonitrene in the exchange is provided by the stereospecific formation of aziridines from *cis*- and *trans*-4-methylpent-2-ene. Dissociation of (**1**) will be facilitated by the stability of both phthalimidonitrene and the aromatic product, as well as by the ability of carbon atoms a and b [see (**1**)] to sustain positive and negative charge respectively. The importance of the last factor is indicated by the failure of the aziridine (**1**; H replacing Ac) to function as a nitrene source.[4] Mechanisms for the exchange involving cleavage of one C–N bond in (**1**) followed by reaction with the trap to give either a dipolar or a biradical intermediate seem less likely. They appear inconsistent either with the efficiency of both nucleophilic and electron deficient olefins as traps, or the stereospecificity of the reaction.

The aziridine (**1**), m.p. 136—140°, is readily prepared (89%) by oxidation of *N*-aminophthalimide[4] in the presence of 2-acetylbenzofuran. It is therefore a convenient source of phthalimidonitrene which is produced under conditions suitable for the preparation of products sensitive to acid, oxidation, and ultraviolet light.

The efficiency of (**1**) as a nitrene source is reduced by its conversion in boiling benzene into the expected[4] rearrangement product (**6**) (15%), m.p. 167—170°.

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† Yields, based on the nitrene source, refer to pure recrystallised products shown to be identical with authentic products derived from phthalimidonitrene generated oxidatively (ref. 2 and 3). 2,2,3-Trichloro-1-phthalimidoaziridine rearranged to chloral phthalylhydrazone under the reaction conditions.

[1] T. L. Gilchrist, C. W. Rees, and E. Stanton, *J. Chem. Soc.* (*C*), 1971, 988.
[2] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc.* (*C*), 1970, 576.
[3] D. W. Jones, unpublished results.
[4] *Cf.* D. W. Jones, *J.C.S. Perkin I*, 1972, 225.