2,4-Dinitrobenzenesulphenylnitrene as a Reactive Intermediate

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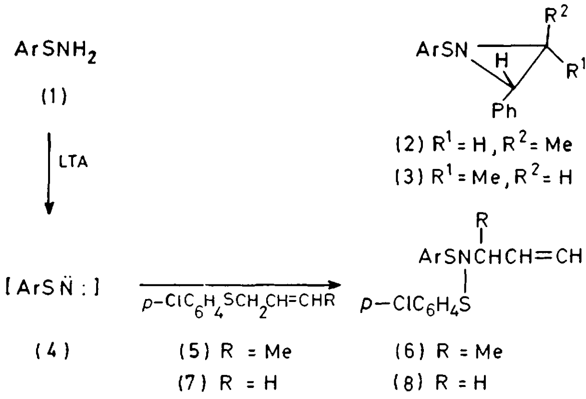
Summary A study of the stereospecificity of addition of the title nitrene, generated by oxidation of the corresponding sulphenamide, to *cis*- and *trans*-propenylbenzene suggests that singlet and triplet nitrene spin states are in equilibrium, with addition of the triplet state to *cis*-propenylbenzene being reversible.

In the preceding communication[1] we reported the formation of aziridines from the oxidation of 2,4-dinitrobenzenesulphenamide (**1**) in the presence of various electron-rich alkenes. We have probed the stereospecificity of this addition to alkenes using *cis*- and *trans*-propenylbenzene. Addition to *trans*-propenylbenzene was apparently stereospecific as judged by n.m.r. spectroscopy giving (**2**) over an eight-fold change in concentration of the alkene (4·7—0·6 M) in dichloromethane.

Oxidation of (**1**) in a benzene solution of *cis*-propenylbenzene (4·7 M), however, gave the *trans*- and *cis*-substituted aziridines (**2**) and (**3**) in a 1 : 1 ratio. This ratio was unchanged when 2·9 and 0·6 M solutions of the *cis*-alkene were used (5 mol. equiv. of alkene in each case).

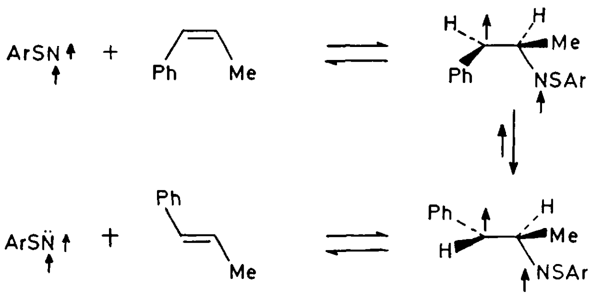


Ar = 2,4-dinitrophenyl. LTA = lead tetra-acetate.

If the intermediate in these oxidations is the sulphenylnitrene $\mathrm{ArS\ddot{N}}$: (**4**), generated in its singlet state, its behaviour contrasts with that of ethoxycarbonylnitrene $\mathrm{EtO_2C\ddot{N}}$:[2a] and cyanonitrene $\mathrm{NC\ddot{N}}$:[2b] in which decay of the singlet [S] to the triplet [T] ground state is characterised by increased non-stereospecific addition to olefins on dilution. In the case of (**4**), one might conclude either that conversion of the singlet into the triplet state is complete at the highest concentration of alkene trap with which it is practicable to carry out the reaction or, alternatively, that reaction of the triplet state of (**4**) with substituted styrenes is fast relative to singlet addition; α-methylstyrene is known to be an excellent triplet scavenger.[3] In either case, addition of the triplet nitrene to *cis*-propenylbenzene would proceed *via* a biradical in which loss of olefin configuration could occur before spin-inversion and aziridine ring formation.

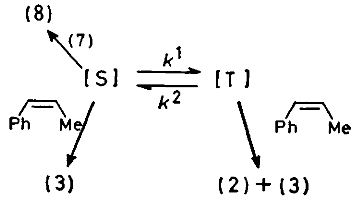
Use of dichloromethane as solvent instead of benzene in the oxidation changes the ratio (**2**) : (**3**) from 1 : 1 to 3 : 1 respectively; again no change in this ratio is apparent on lowering the *cis*-propenylbenzene concentration from 4·7 to 2·9 M† (5 mol. equiv. alkene) although a small change towards a larger amount of (**2**) was detectable at lower concentration (0·6 M) using 1 mol. equiv. of alkene.

These ratios of (**2**) : (**3**) were determined after removal of excess of *cis*-alkene and acetic acid by chromatography over neutral alumina; appropriate control experiments showed that the ratios were not affected by this chromatography.‡ However, g.l.c. examination of the recovered alkene revealed that the *cis*-propenylbenzene underwent conversion in part into the *trans*-isomer during the reaction. Thus using 1 mol. equiv. of propenylbenzene which was 98 : 2 *cis* : *trans* in dichloromethane (0·6 M) gave a recovered alkene sample having a ratio of 1 : 4 *cis* : *trans*. Neither acetic acid, lead tetra-acetate, nor neutral alumina effected this conversion when the oxidation reaction and work up conditions were simulated. Presumably it is isomerisation of the *cis*-alkene by reversible addition of the nitrene (**4**) (Scheme 1) which is responsible for the small increase in the ratio (**2**) : (**3**) from the oxidation of (**1**) in the presence of 1 mol. equiv. of *cis*-propenylbenzene at 0·6 M referred to above.



Scheme 1. Ar = 2,4-dinitrophenyl

Allyl sulphides are also excellent traps for this sulphenylnitrene. Oxidation of (**1**) in the presence of *p*-chlorophenyl but-2-enyl sulphide (**5**) gave the *N*-arylthiosulphenamide (**6**), presumably by initial attack of singlet (**4**) on the sulphur atom in (**5**) followed by [2,3] sigmatropic rearrangement.[4] Addition of allyl *p*-chlorophenyl sulphide (**7**) (0·5 mol. equiv.) to a benzene solution of (**1**) in the presence of *cis*-propenylbenzene (2·9 M; 5 mol equiv.) changed the ratio of (**2**) : (**3**) from 1 : 1 to 5 : 2. This confirms the efficacy of this allyl sulphide as a trap for the nitrene (**4**) since the sulphenamide (**8**) is the major product [the yield of (**8**) is 3 times that of (**2**) + (**3**) from n.m.r. examination] despite the 10-fold excess of *cis*-propenylbenzene. If it is accepted that only the singlet state of (**4**) reacts with the allyl sulphide (**7**)[5] then at least some of the aziridine (**3**) must be derived from this singlet state. This conclusion contradicts that drawn earlier from the absence of an effect of dilution on the ratio of (**2**) : (**3**). The conflict may be resolved if it is assumed that singlet and triplet states of the nitrene (**4**) are in equilibrium and both react with *cis*-propenylbenzene (Scheme 2). The effect of adding an



Scheme 2

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† Use of dibromomethane in place of dichloromethane in this experiment (2·9 M) gave an identical ratio of (**2**) : (**3**). Dibromomethane is a heavy atom-containing solvent which is known to accelerate the rate of singlet to triplet decay in nitrenes (see refs.2).

‡ On attempted chromatography using basic alumina, (**2**) suffered decomposition at a significantly faster rate than (**3**) which was convenient for isolation of a pure sample of the latter, m.p. 109—110 °C (from EtOH).

allyl sulphide is to divert some of the singlet state from reaction to form (**3**)§ thus accounting for the apparent increase in the ratio of (**2**) : (**3**).¶

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§ With appropriate values of k_1 and k_2.

¶ It may be that [T] gives exclusively (**2**); the effect of increasing the allyl sulphide concentration on the ratio of (**2**) : (**3**) would support this view.

[1] R. S. Atkinson and B. D. Judkins, *J.C.S. Chem. Comm.*, preceding communication.
[2] (a) W. Lwowski, *Angew. Chem. Internat. Edn.*, 1967, **6**, 897; (b) A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1967, **89**, 3184.
[3] W. Lwowski and J. S. McConaghy, *J. Amer. Chem. Soc.*, 1967, **89**, 2357.
[4] Compare R. S. Atkinson and S. B. Awad, *J.C.S. Perkin I*, 1977, 346.
[5] The singlet state of carbenes is thought to be that which reacts with sulphides by attack on sulphur; W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, 1969, **91**, 2786; W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *ibid.*, p. 5164.