2,4-Dinitrobenzenesulphenylnitrene: Addition to (*Z*)- and (*E*)-1-Phenylpropene

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Oxidation of 2,4-dinitrobenzenesulphenamide (1) with lead tetra-acetate in the presence of (*Z*)-1-phenylpropene gives a *ca.* 3:1 mixture of *cis*- and *trans*-aziridines (3) and (4), respectively. This ratio is unchanged over a ten-fold decrease in concentration of (*Z*)-1-phenylpropene. The ratio of compounds (3) : (4) is unaffected by carrying out the oxidation in the presence of 1,1-diphenylethene, 2-phenylpropene or oxygen (triplet traps), although both the last-named alkenes react preferentially with the intermediate(s) generated in the reaction. The ratio (3) : (4) *is* affected by carrying out the oxidation in the presence of an allyl aryl sulphide, a particularly effective singlet nitrene trap. It is concluded that at least two intermediates are involved in the addition to (*Z*)-1-phenylpropene, one of which is a singlet nitrene; however the other is not the triplet nitrene.

Partial isomerisation of the (*Z*)-1-phenylpropene to (*E*)-1-phenylpropene in these reactions is attributed to the reversible addition of the 2,4-dinitrobenzenesulphenamidyl radical, 2,4-$(NO_2)_2PhS\dot{N}H$ to the (*Z*)-alkene

THE spin-state of a carbene or nitrene is commonly determined by the stereospecificity of its addition to alkenes. Thus, whilst addition of the singlet state is stereospecifically *cis* with respect to the alkene ($_2\pi_s + {}_\omega 2_a$), the triplet state adds non-stereospecifically *via* a biradical species.

Using this criterion, the most commonly investigated nitrene, ethoxycarbonylnitrene $EtO_2C\ddot{N}$:, has been found to have a triplet ground state. Thus, this nitrene, generated initially in its singlet state, adds increasingly non-stereospecifically to *cis*-alkenes (to give aziridines) with decreasing concentration of the *cis*-alkene trap as more of the nitrene decays to its triplet ground state before addition.[1]

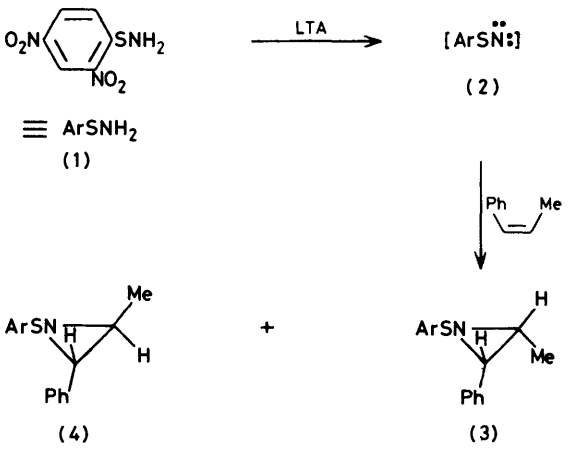
In practice, only a limited number of nitrenes have been trapped intermolecularly by alkenes and, of these, most have singlet ground states. These include (a) a large family of *N*-nitrenes [2] where the second nitrogen is invariably part of a heterocyclic ring, (b) a limited number of *O*-nitrenes,[3] and (c) some iminonitrenes ROC(=NR')$\ddot{N}$:.[4]

We recently reported that oxidation of 2,4-dinitrobenzenesulphenamide (1) with lead tetra-acetate (LTA) in the presence of electron-rich alkenes gives rise to aziridines in good yields.[5] Curiously, although *o*-nitrobenzenesulphenamide yielded analogous aziridines in the above reaction, no aziridines were isolated when *p*-nitrobenzenesulphenamide was used.

To probe into the spin-state of the presumed nitrene intermediate (2) in the formation of these aziridines, we have investigated the oxidation of the sulphenamide (1) in the presence of *cis*-1-phenylpropene (Scheme 1).[6]

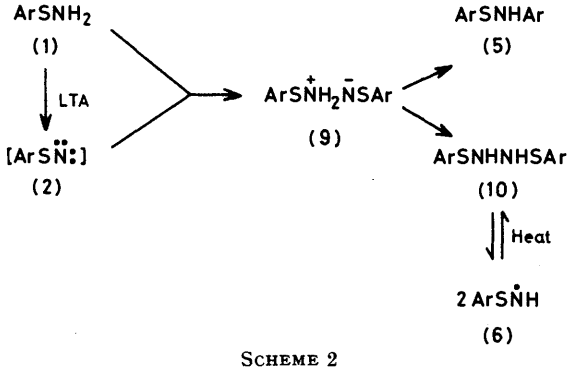
When LTA is added to a solution of the sulphenamide (1) and *cis*-1-phenylpropene (method A), an additional product besides the aziridines (3) and (4) obtained after chromatography on basic alumina is the diarylsulphenamide (5). Formation of compound (5) is believed to be the eventual result of attack of the sulphenylnitrene (2) on unchanged sulphenamide (1) (Scheme 2).

We reasoned that the yield of this by-product could be reduced if the concentration of starting sulphenamide



SCHEME 1

were minimised. In practice this could be achieved by the gradual addition of equimolar amounts of LTA and sulphenamide (1) to a solution of the alkene. In the solid state, dry, acetic-acid free LTA and sulphenamide



SCHEME 2

(1) do not react even when powdered together.† Thus, addition of small quantities of this solid mixture to a solution of the alkene provides a convenient means of

† *Caution.* This procedure has not been tested with more than a total of 500 mg of solid.

minimising the concentration of the sulphenamide (1) (method B).

The variation in the ratio of aziridines (3) and (4) obtained using methods A and B together with changes in solvent, alkene, and alkene concentration are shown in Table 1. For the determination of these ratios (for details see the Experimental section), the methyl doublets at δ 1.20 and 1.60 [from (3) and (4), respectively] in the n.m.r. spectra of the crude reaction products, were measured by integration. Yields of aziridines (3) and (4) were determined after chromatography through neutral alumina which also separated unchanged *cis*-1-phenylpropene.

TABLE 1

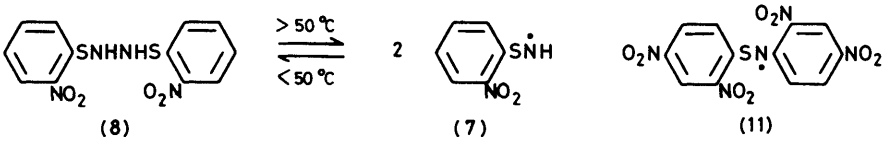
Reaction conditions and products for oxidation of sulphenamide (1) with lead tetra-acetate in the presence of *cis*- and *trans*-1-phenylpropene

Run no.	Method (see text)	Solvent	Alkene concentration (mol %)	1-Phenylpropene	Alkene (mol equiv.)	Aziridine ratio (3) : (4)	Aziridine yield (%)	Ratio *cis* : *trans* recovered 1-phenylpropene [a]
1	B	$CHCl_3$	5	*cis*	5	77 : 23 [b]	75	98 : 2
2	B	$CHCl_3$	1.1	*cis*	1.1	76 : 24	40	92 : 8
3	B	$CHCl_3$	0.67	*cis*	5	74 : 26	69	98 : 2
4	A	$CHCl_3$	5	*cis*	5	54 : 46	49	96 : 4
5	B	Benzene	5	*cis*	5	74 : 26	52	
6	A	Benzene	5	*cis*	5	53 : 47	27	
7	B	CH_3CN	3.2	*cis*	5	57 : 43	27	
8	A	CH_3CN	3.2	*cis*	5	57 : 43	13	
9	B	MeOH	2.5	*cis*	5	60 : 40	13	
10	B	$CHCl_3$	4.27 (*cis*) 0.71 (*trans*)	*cis* and *trans*	4.27 (*cis*) 0.71 (*trans*)	41 : 59 [c]	84	
11	A	$CHCl_3$	2.5	*trans*	2.5	<2 : >98	71	
12	B	$CHCl_3$	2.25	*trans*	2.25	<2 : >98	84	
13	B	$CHCl_3$	1.13	*trans*	1.13	<2 : >98	81	

[a] Ratio *cis* : *trans* of starting 1-phenylpropene was 98 : 2. [b] This ratio was not affected when O_2 was bubbled through the solution throughout the addition. [c] This ratio is corrected to account for the *trans*-aziridine (4) which is formed using *cis*-1-phenylpropene: since less than 1 mol equiv. of *trans*-1-phenylpropene is used, the calculated reactivity ratio (8.6 : 1 *trans* : *cis*) is less than the actual ratio.

control experiments established that this *cis*→*trans* isomerisation occurred during the reaction. Thus the *cis*-alkene was not isomerised by LTA or by alumina chromatography or by acetic acid (a by-product in the the LTA oxidation).

The major part of the difference in *cis* : *trans* aziridine ratios obtained by methods A and B (compare runs 1 and 4 and runs 5 and 6) can be attributed to this isomerisation of the *cis*-1-phenylpropene during the addition in method A, since a control experiment (run 10) using a mixture of the *cis*- and *trans*-alkenes shows that the *trans*-alkene is at least 8.6 times more reactive than the *cis*-alkene towards the nitrene.



SCHEME 3

In the addition to *cis*-1-phenylpropene, the appearance among the products of the aziridine (4), containing the alkene residue with inverted configuration, is usually taken to be diagnostic of triplet character in the intermediate nitrene. Runs 1, 2, and 3, however, indicate that nitrene (2) does not respond in the classical way expected for a nitrene with a triplet ground state. Thus the stereoselectivity is not significantly changed over an almost ten-fold change in the concentration of alkene.

An unexpected discovery was that the ' unchanged ' *cis*-1-phenylpropene recovered from these reactions had been partially isomerised to *trans*-1-phenylpropene when method A was used (Table 1). Using method B this isomerisation was negligible except where only 1.1 mol equiv. of *cis*-alkene were used (run 2). Appropriate

We believe that the species which brings about the alkene isomerisation is the 2,4-dinitrobenzenesulphenamidyl radical (6) (Scheme 2). Thus, oxidation of sulphenamide (1) by LTA in the absence of 1-phenylpropene and examination of the chloroform solution by e.s.r. spectroscopy reveals a triplet of lines which can be assigned to radical (6). Not only are the g (2.0075) and A (11.5 G) values very close to those corresponding to compound (7) ($g = 2.0076$, $A = 11$ G), which have previously been reported,[7] but the signal intensifies remarkably above *ca.* 30 °C and is diminished when the temperature is lowered again. This behaviour, reproduced by subsequent heating and cooling, is also characteristic of compound (7) and has been attributed to the reversible dissociation of the dimer (8) (Scheme 3).

We have previously considered a route [5] for the genesis of compound (5) (Scheme 2) which includes the ylide (9); this, by proton transfer, could give the analogous dimer (10) of the sulphenamidyl radical (6). Attempts to isolate compound (10) from the reaction mixture have not been successful, even when 0.5 mol equiv. of LTA was used. The only product isolated (in poor yield) before chromatography was the diarylsulphenamide (5).

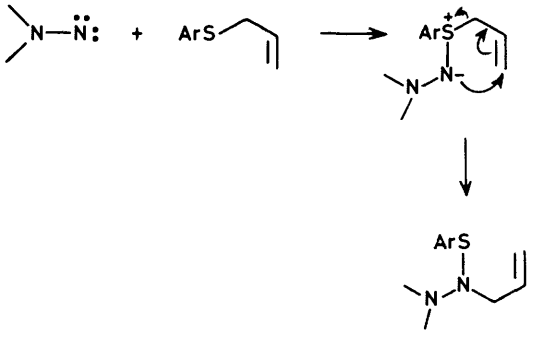
Since the diarylsulphenamide (5) is a product in the LTA oxidation of compound (1), we also obtained the e.s.r. spectrum of the derived diarylsulphenamidyl radical (11) by treatment of a suspension of (5) (10 mg) in chloroform with LTA (2 mg). This spectrum, which has a triplet [$g = 2.0064$ and $A(^{14}N)$ 9.0 G], resembles the spectra of analogous diarlysulphenamidyl radicals,[8] but is clearly different from that of the sulphenamidyl radical (6) above, and is not detectable in the reaction mixture in which (6) is found.

Identification of the radical (6) in the reaction mixture does not prove, of course, that it is this species which adds reversibly to *cis*-1-phenylpropene and brings about its isomerisation, but the fact that the addition is reversible indicates that the (presumed) radical species which is responsible must be highly stabilised. Certainly, isomerisation brought about by the radical (6) seems more likely than our previous suggestion [6] of reversible addition of the triplet nitrene. As well as being unprecedented, this latter explanation cannot account for the result in run 2 (Table 1) where only 1.1 mol equiv. of alkene were used: here there is no loss of stereoselectivity [no increased proportion of aziridine (4) formed *via* the triplet state] and yet the alkene undergoes appreciably more isomerisation.

Returning to a consideration of the mechanism of addition of nitrene (2) to *cis*-1-phenylpropene, we have assumed (Scheme 2) that in the formation of the diarylsulphenamide (5) the initial attack of the singlet nitrene takes place on the nitrogen of the sulphenamide (1). Our previous results using *N*-nitrenes,[2] which have singlet ground states, suggest that divalent sulphur in aryl allyl sulphides is a particularly good *singlet* trap * when the aryl group is not substituted with electron-withdrawing groups [*cf.* sulphenamide (1)]. The function of the allyl group is to divert the initially formed sulphenimide to a stable sulphenamide *via* a [2,3]-sigmatropic rearrangement (Scheme 4).

Oxidation of the sulphenamide (1) with LTA in the presence of *trans*-but-2-enyl 4-chlorophenyl sulphide (12) gave an orange gum in 74% yield, identified as the sulphenamide (13) (Scheme 5).

The assignment of structure (13) to this product was supported by its spectral data and also by the isolation of compound (14) after treatment with dry hydrogen chloride in diethyl ether. Cleavage of both S–N bonds was expected, giving the amine salt (15) and the two sulphenyl chlorides (16) and (17). Preferential addition of *p*-chlorobenzenesulphenyl chloride (16) to the alkene double-bond of (15) would be expected because of the stability of an intermediate episulphonium salt. Addition of this sulphenyl chloride is probably as indicated in structure (14), by analogy with a similar example.[9] The dinitrobenzenesulphenyl chloride formed was trapped by methanol to give the known crystalline sulphenate ester (18) in 82% yield.



SCHEME 4

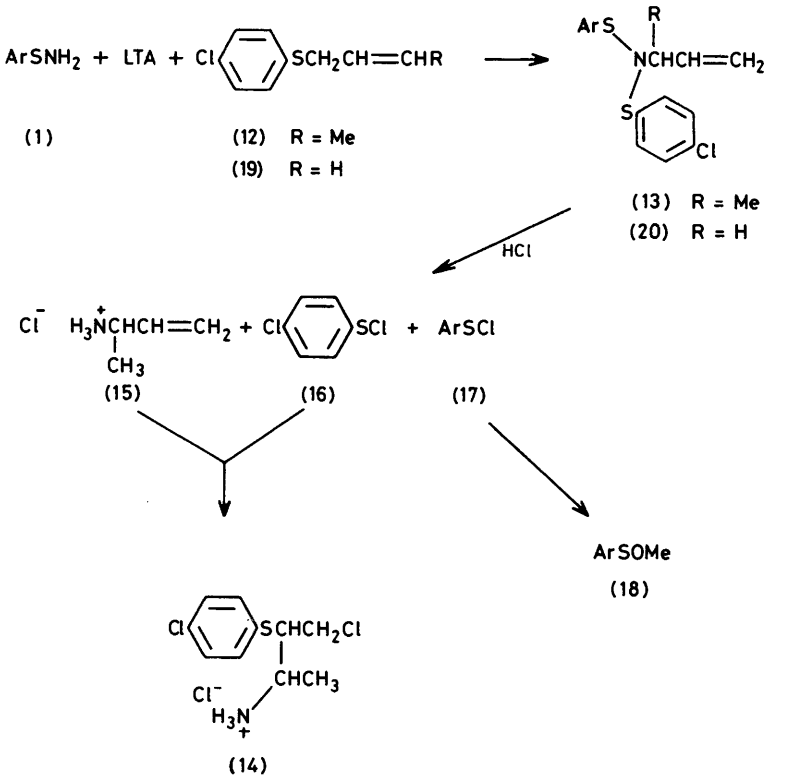
The effect of addition of *ca.* 0.5 mol equiv. of the allyl aryl sulphide (19) is shown in Table 2 (runs 1 and 2): the ratio of *cis* : *trans*-aziridines obtained alters from 77 : 23 to 66 : 34. Despite the ten-fold excess of *cis*-1-phenylpropene used, and the fact that only 0.5 mol equiv. of sulphide (19) are present, the yield of the sulphenamide (20) (from n.m.r.) is three times that of the aziridines (3) and (4); this shows the efficacy of the sulphide in trapping the intermediate nitrene.

To accommodate the effect of added sulphide (19) and the absence of any dilution effect on the ratio of (3) : (4) (Table 1, runs 1, 2, and 3), it is necessary to make two fundamental changes to the usual scheme for production of the triplet nitrene (Scheme 6); (*a*) the singlet and triplet states must be in rapid equilibrium and their interconversion must be faster than their respective reactions with the alkene, and (*b*) the triplet nitrene must be generated, at least in part, from oxidation of the sulphenamide (1) by an alternative route which by-passes the singlet nitrene. Thus it can be shown that [S]/[T] is not affected by the reaction of the singlet with the sulphide (19) if the singlet is the only source of the triplet.

A test for the validity of Scheme 6 would be the observation of an *increase* in the stereospecificity of nitrene addition to the alkene as the result of the introduction of a specific *triplet* trap. In the event, the addition of 1,1-diphenylethene to *cis*-1-phenylpropene had no significant effect on the ratio of aziridines (3) : (4) (run 3, Table 2). Examination of the n.m.r. spectrum of the crude product mixture indicated that 1,1-diphenylethene is *ca.* 1.7 times as reactive as *cis*-1-phenylpropene, based on the ratio of the respective aziridines (21) : [(3) and (4)] obtained.

Likewise, the presence of *ca.* equimolar amounts of 2-phenylpropene in the reaction mixture with *cis*-1-phenyl-

* The reactions of carbenes with sulphides on sulphur have been shown to be a reaction of the singlet state. Refs. W. Ando, T. Yagihara, S. Tonzune, and T. Magita, *J. Am. Chem. Soc.*, 1969, **91**, 2786; W. Ando, K. Nakayama, K. Ichibori, and T. Magita, *ibid.*, p. 5164.



SCHEME 5

propene had no significant effect on the aziridine ratio (Table 2, run 4). Again, more aziridine was formed from 2-phenylpropene and n.m.r. integration gave a reactivity of *ca.* 1.5 times that of *cis*-1-phenylpropene. The triplet state of ethoxycarbonylnitrene is efficiently trapped by 2-phenylpropene.[10] Significantly, the product is not an aziridine but 3-ethoxycarbonylamino-2-phenylprop-1-ene (22), probably formed by H-atom transfer in the 1,3-diradical intermediate. No products other than aziridines were observed in the n.m.r. spectrum of the crude reaction products from the above experiment.

Both 1,1-diphenylethene and 2-phenylpropene are expected to be superior triplet traps to *cis*-1-phenylpropene, and the fact that neither has any effect on the ratio of aziridines (3) : (4), in spite of being *more* reactive than the latter alkene, is a strong argument against any involvement of the triplet nitrene at all.

Another good triplet trap is oxygen, but again the ratio of aziridines (3) : (4) was unchanged when oxygen was continuously bubbled through the solution under the conditions of run 1, Table 1.

To summarise, therefore, it appears that oxidation of the sulphenamide (1) generates at least two reactive intermediates. One adds stereospecifically to *cis*-1-phenylpropene to give the aziridine (3), but reacts preferentially with allyl aryl sulphide (19) to give the sulphenimide (20). These properties are not inconsistent with those expected for singlet nitrene (2). The other intermediate adds non-stereospecifically to the alkene, but is not the triplet nitrene.

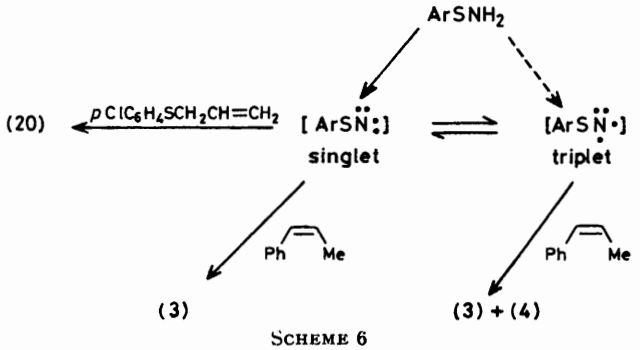
An important factor to be borne in mind when considering the nature of this unknown species is that aziridines are only obtained when the arylsulphenamide bears a nitro-group in the *ortho*-position. The *o*-nitro group

TABLE 2

Effects of various additives on the ratio of aziridines (3) and (4) produced in the oxidation of the sulphenamide (1) in chloroform in the presence of *cis*-1-phenylpropene

Run no.	Method used (see text)	*cis*-1-Phenylpropene concentration (mol %)	*cis*-1-Phenylpropene (mol equiv.)	Additive	Ratio of aziridines (3) : (4)
1	B	5	5	—	77 : 23 •
2	B	5	5	*p*ClC$_6$H$_4$CH$_2$CH=CH$_2$ (0.5 mol equiv.)	66 : 34
3	B	2.5	2.5	Ph$_2$C=CH$_2$ (1.6 mol equiv.)	76 : 24
4	B	2.75	2.75	2-Phenylpropene (2.25 mol equiv.)	77 : 23

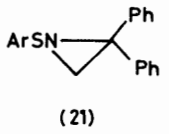
could intercept the presumed lead-containing intermediate in the oxidation to give compound (23), or could trap the nitrene intramolecularly at nitrogen [compound (24)] or sulphur [compound (25)] (Scheme 7). Any one of these species could react non-stereospecifically with *cis*-1-phenylpropene *via* a dipolar intermediate within which



SCHEME 6

carbon–carbon bond rotation could take place before aziridine ring-closure.

Runs 7, 8, and 9 (Table 1) were carried out in acetonitrile and methanol specifically to test the effects of polar solvents on the ratios of aziridines (3) and (4) obtained. Unfortunately, in both cases, the yields of aziridines were poor, and in both cases the major product was an unidentified red polymeric material. Although



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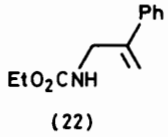

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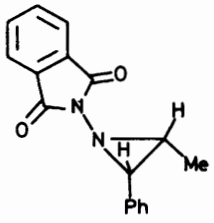
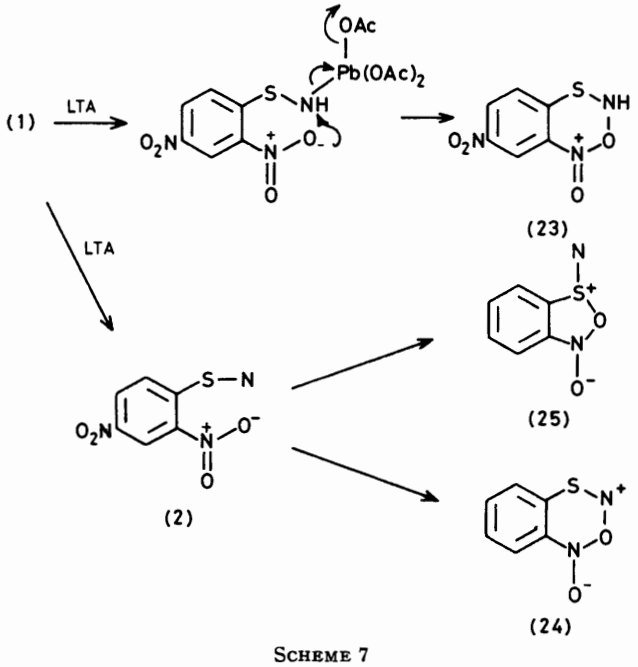


(26)

there is some loss of stereoselectivity, as would be expected from a longer lifetime for a dipolar intermediate, it is difficult to draw reliable conclusions in view of the poor yields of aziridines. It is interesting to note that the yield of the sulphenamide (20) obtained when oxidation of the sulphenamide (1) is carried out in the presence of the sulphide (19) in acetonitrile is nearly quantitative.

As can be seen from Table 1 (runs 11, 12, and 13), oxidation of the sulphenamide (1) with LTA in the presence of *trans*-1-phenylpropene gives only the aziridine (4) under all conditions used. There is no evidence here, therefore, for anything other than concerted nitrene addition to *trans*-1-phenylpropene, but again it is possible that the nitrene involved has structure (25) rather than (2). Moreover, there remains the possibility that compound (23) or (24) could react stereospecifically with *trans*-1-phenylpropene but non-stereospecifically with *cis*-1-phenylpropene.

For comparison, we have oxidised *N*-aminophthalimide in the presence of *cis*-1-phenylpropene (1 mol equiv.). The only product isolated was the *cis*-aziridine (26) whose stereochemistry was established by the coupling constant (J 8 Hz) between the two aziridine ring protons: none of the *trans*-aziridine was detected in the crude reaction mixture. Thus, *N*-phthalimidonitrene reacts apparently stereospecifically with *cis*-1-phenylpropene, as expected for its singlet ground state.[11]



SCHEME 7

EXPERIMENTAL

For details of instrumentation and general experimental directions see ref. 5. E.s.r. spectra were obtained using a Bruker ER 200 spectrometer. (*Z*)-1-Phenylpropene was prepared by a modification of the method of Coussement *et al.*[12] *via* decarboxylation of 2-methylcinnamic acid with copper powder and quinoline, and was obtained with some quinoline by distillation under reduced pressure after each 3 h heating period at 240 °C. After removal of quinoline by extraction with acid, the (*Z*)-alkene was purified by passage through a column of activated alumina to remove traces of a copper-containing species (shown to be present by e.s.r. spectroscopy) followed by distillation under reduced pressure. Ether refers to diethyl ether throughout.

Oxidation of 2,4-Dinitrobenzenesulphenamide (1) *in the Presence of* (Z)-1-*Phenylpropene.—Method A.* Typically, as in run 1, Table 1, the sulphenamide (1) (146 mg) and (*Z*)-1-phenylpropene (400 mg) were vigorously stirred in chloroform (5.4 ml; freshly distilled from phosphorus pentaoxide) while powdered lead tetra-acetate (LTA) (300 mg) was

added over a period of 6 min. After stirring for an additional 5 min, the solid lead diacetate was separated and the chloroform evaporated under reduced pressure keeping the temperature below 35 °C. After measurement of the relative intensities of the methyl doublets at δ 1.60 and 1.20 in its n.m.r. spectrum, the residue was adsorbed on to neutral alumina (Woelm; Activity IV) and added to the top of a small column of the same alumina made up in light petroleum (b.p. 60—80 °C). Residual 1-phenylpropene was eluted with light petroleum and the aziridines (3) and (4) with light petroleum–ether (5 : 3) as a canary yellow band. The yield of aziridines was determined after evaporation of the solvent under reduced pressure. Before re-examination by n.m.r. spectroscopy, it was convenient to 'chase off' traces of light petroleum by addition of benzene (2 ml) followed by re-evaporation. The ratio of aziridines, (3) : (4), was checked by n.m.r. not only from the ratio of doublets referred to above but also from the ratio of the doublet at δ 3.40 [*J* 7.3 Hz (aziridine ring 3-H in (3)] to the multiplet at δ 3.0—2.5 [all other aziridine-ring H in (3) and (4)]. In no case was there any significant difference in ratios (3) : (4) from measurements on crude and chromatographed material.

Other runs in Table 1 were carried out using benzene (dried over sodium wire), acetonitrile (freshly distilled from phosphorus pentaoxide) or methanol using sulphenamide (1) (146 mg) and (*E*)- or (*Z*)-1-phenylpropene at the concentrations indicated.

Using method B. The procedure used was exactly as described above except that solid sulphenamide (1) and LTA were intimately mixed and the solid mixture added to a solution of the 1-phenylpropene in the appropriate solvent over a period of 6 min.

Reaction of Sulphenamide (1) *with* (E)-*But-2-enyl 4-Chlorophenyl Sulphide* (12) *and Lead Tetra-acetate.*—The sulphenamide (1) (450 mg) and (*E*)-but-2-enyl 4-chlorophenyl sulphide (12) (600 mg) were stirred in dichloromethane (3.5 ml) while powdered LTA (1.09 g) was added in portions during 10 min. After a further 30 min, the precipitated lead diacetate was separated, the solution evaporated and the residue chromatographed over basic alumina. Elution with light petroleum–ether (9 : 1) gave unchanged sulphide (12). Further elution with ether gave *N*-1-methylallyl-*N*-(4-chlorophenylthio)-2,4-dinitrobenzenesulphenamide (13) (640 mg, 74%) as an orange gum; $\nu_{max.}$ 3 100w, 1 590s, 1 470m, 1 340s, and 1 300s cm^{-1}; δ($CDCl_3$) 9.0 (d, *J* 2 Hz, aryl 3-H), 8.35 (dd, *J* 2 and 9 Hz, aryl 5-H), 7.80 (d, *J* 9 Hz, aryl 6-H), 7.30 (AA'BB', 4 × aryl H), 6.1—5.7 (m, C*H*=CH_2), 5.3—5.0 (m, CH=CH_2), 4.05 (m, NC*H*), and 1.35 (d, *J* 7 Hz, Me). This sulphenamide (13) was characterised by its reaction with hydrogen chloride as follows: the sulphenamide (680 mg) was dissolved in dry ether (25 ml) and dry hydrogen chloride gas passed into the ice-cooled mixture for 0.5 h. After a further 1 h at 0 °C, the white solid which had formed was separated and identified as 3-*chloro*-2-(4-*chlorophenylthio*)-1-*methylpropylamine hydrochloride* (14) (215 mg, 45%), m.p. 131—134 °C (from light petroleum–acetone) (Found: C, 41.9; H, 4.9; N, 4.9. $C_{10}H_{14}Cl_3NS$ requires C, 41.9; H, 4.9; N, 4.9%); $\nu_{max.}$ 3 200—2 800br, 1 600m, 1 520, 1 100s, and 830s cm^{-1}; δ($CDCl_3$) 8.80 (s br, NH_3), 7.40 (AA'BB', 4 × aryl H), 4.10—3.40 (m, 4 × aliphatic H), and 1.57 (d, *J* 6 Hz, Me).

The ether solution above, after removal of the hydrochloride (14), was evaporated and then dissolved in dry ether (10 ml). This solution was added slowly to a stirred mixture of methanol (1 ml), pyridine (0.5 ml), and dry ether (10 ml) during 10 min. After a further 10 min, the mixture was filtered, evaporated and the residue crystallised from methanol to give 2,4-dinitrophenyl methanesulphenate (18) (310 mg, 81%) as yellow crystals, m.p. 120—122 °C (lit.,[13] 125 °C); δ ($CDCl_3$) 9.05 (d, *J* 2 Hz, aryl 3-H), 8.50 (dd, *J* 2 and 9 Hz, aryl 5-H), 7.90 (d, *J* 9 Hz, aryl 6-H), and 4.0 (s, Me).

Reaction of Sulphenamide (1) *with Allyl* p-*Chlorophenyl Sulphide and Lead Tetra-acetate (in the Presence of* (Z)-1-*Phenylpropene).*—Sulphenamide (1) (146 mg) and LTA (300 mg) were intimately mixed in the solid state and added to a solution containing allyl *p*-chlorophenyl sulphide (72 mg) and (*Z*)-1-phenylpropene (400 mg) in dry acetonitrile (5.4 ml). After separation of lead diacetate and evaporation of the solvent, n.m.r. indicated the absence of any signals from aziridines (3) or (4). Chromatography over neutral alumina (see method A above) gave (*Z*)-1-phenylpropene, and elution with light petroleum–ether (5 : 3) gave N-*allyl*-N-(4-*chlorophenylthio*)-2,4-*dinitrobenzenesulphenamide* (20) as an oil (130 mg, 90% based on sulphide used), which crystallised on titration with methanol. Recrystallisation gave yellow plates, m.p. 75—78 °C (from chloroform–ethanol) (Found: C, 45.4; H, 3.1; N, 10.55. $C_{15}H_{12}ClN_3O_4S_2$ requires C, 45.3; H, 3.05; N, 10.55%); $\nu_{max.}$ 1 590s, 936w, 915w, 825m, 806w, 740w, and 732w cm^{-1}; δ($CDCl_3$) 8.99 (d, *J* 2 Hz, aryl 3-H), 8.13 (dd, *J* 2 and 9 Hz, aryl 5-H), 7.58 (d, 9 Hz, aryl 6-H), 7.4—7.0 (AA'BB', 4 × aryl H), 6.0—5.4 (m, C*H*=CH_2), 5.2—4.9 (m, CH=CH_2), and 3.93 (d, *J* 6 Hz, CH_2CH=CH_2).

Oxidation of Sulphenamide (1) *in the Presence of* (Z)-1-*Phenylpropene and* 1,1-*Diphenylethene.*—Oxidation of sulphenamide (1) (146 mg) with LTA (300 mg) in the presence of (*Z*)-1-phenylpropene (200 mg) and 1,1-diphenylethene (200 mg) in chloroform (5.4 ml) was carried out according to the general procedure described above, using method B. Examination of the n.m.r. spectrum of the crude product after separation of lead diacetate and evaporation of the solvent showed that the ratio of aziridine (21) to aziridines (3) and (4) was *ca.* 5 : 3; this was established from the ratio of the singlet at δ 2.83 [aziridine ring H in (21)] to the doublets at δ 1.60 and 1.20 [Me groups in (3) and (4) respectively]. The ratio of these latter peaks was unchanged from that obtained in an experiment carried out as above in the absence of 1,1-diphenylethene (Table 1, run 1).

Oxidation of Sulphenamide (1) *in the Presence of* 1,1-*Diphenylethene.*—A powdered mixture of sulphenamide (1) (73 mg) and LTA (150 mg) was added in portions during 5 min to a solution of 1,1-diphenylethene (200 mg) in chloroform (2.7 ml). After stirring for a further 5 min the lead diacetate was separated and the solvent removed. Trituration of the residue with light petroleum and crystallisation of the solid obtained from chloroform–methanol gave N-(2,4-*dinitrophenylthio*)-2,2-*diphenylaziridine* (21) as yellow needles, m.p. 127—129 °C (Found: C, 60.55; H, 3.85; N, 10.6. $C_{20}H_{15}N_3O_4S$ requires C, 61.05; H, 3.85; N, 10.7%); $\nu_{max.}$ 1 590s, 1 585sh, 928w, 914m, 743m, and 700 cm^{-1}; δ($CDCl_3$) 8.8 (d, *J* 2 Hz, aryl 3-H), 8.4 (d, *J* 9 Hz, aryl 6-H), 8.2 (dd, *J* 2 and 9 Hz, aryl 5-H), 6.9 (s, 10 × aryl H), and 2.84 (s, 2 × aziridine-ring H).

Control Experiments.—(i) (*Z*)-1-Phenylpropene [100 mg; 98 : 2 (*Z*) : (*E*)] and acetic acid (2 drops) were stirred in chloroform (1.5 ml) at room temperature for 0.5 h. Ether (10 ml) was added and the mixture extracted with aqueous sodium carbonate (8%), washed with water and dried.

G.l.c. of the solution (3% OV 225; 75 °C) revealed no change in the proportion of the (*E*)-alkene present.

(ii) (*Z*)-1-Phenylpropene [100 mg; 98 : 2 (*Z*) : (*E*)] and LTA (100 mg) were dissolved in dichloromethane (1 ml) and stirred at room temperature for 0.5 h. Ether (3 ml) was added and the solution allowed to percolate through a small column of neutral alumina. G.l.c. of the resulting solution revealed no change in the proportion of (*E*)-alkene present.

(iii) A mixture of the aziridines (3) and (4) 250 mg; ratio 1 : 1), allyl 4-chlorophenyl sulphide (19) (220 mg) and LTA (310 mg) were stirred in dichloromethane (2 ml) at room temperature for 2 h. The solution was percolated through a small column of neutral alumina and evaporated. N.m.r. spectroscopy of the residue revealed no change in the ratio of the aziridines (3) and (4).

(iv) A solution of aziridines (3) (30 mg) and (4) (30 mg) in deuteriochloroform (0.3 ml) containing LTA (18 mg) was monitored by n.m.r. spectroscopy. There was no evidence of change in the ratio (3) : (4) or loss of intensity of their signals over a period of 4 h.

Oxidation of N-*Aminophthalimide in the Presence of* (Z)-1-*Phenylpropene.*—*N*-Aminonaphthalimide (0.81 g) and (*Z*)-1-phenylpropene (0.6 g) were dissolved in dichloromethane (4 ml) (*N*-aminophthalimide was not completely soluble) and powdered LTA (2.2 g) added during 15 min at room temperature. After a further 1 h, the lead salts were separated and the residual solution evaporated and chromatographed over neutral alumina (25 g). Elution with light petroleum yielded unchanged alkene. Further elution with light petroleum–ethyl acetate (1 : 1) afforded cis-2-*methyl*-3-*phenyl*-1-*phthalimidoaziridine* (26) (270 mg, 20%) as pale yellow crystals (from ethanol), m.p. 81—82 °C (Found: C, 73.4; H, 5.05; N, 10.1. $C_{17}H_{14}N_2O_2$ requires C, 73.4; H, 5.1; N, 10.1%); $\nu_{max.}$ 1 765w, 1 730s, 1 700s, 1 610w, 1 160m, 1 030m, 1 020m, 895s, and 710s cm^{-1}; $\delta(CDCl_3)$ 7.8—7.2 (m, 9 × ArH), 3.70(d, *J* 8.0 Hz, aziridine 3-H), 2.95 (dq, *J* 6 and 8 Hz, aziridine 2-H), and 1.25 (d, *J* 6 Hz, Me).

Identification of the 2,4-*Dinitrobenzenesulphenamido-radical* (6) *in the Lead Tetra-acetate Oxidation of Sulphenamide* (1).—The dinitrobenzenesulphenamide (1) (73 mg) was suspended in chloroform (2.5 ml) and treated with LTA (150 mg) in small portions. After stirring for a further 5 min, the precipitated material was separated and the red-brown solution examined by e.s.r. spectroscopy. Three intense lines which could be assigned to compound (6) appeared when the temperature was raised above 30 °C [g = 2.0075, $A(^{14}N)$ = 11.5 G] but their intensity was reduced almost to zero below 17 °C. Above 47 °C, the intensity of the signals slowly diminished as a result of decomposition.

For comparison, the e.s.r. spectrum of the *N*-(2,4-dinitrophenyl)-2,4-dinitrobenzenesulphenamidyl radical (11) was taken for a solution obtained by treatment of a suspension of compound (5) (10 mg) in chloroform (1 ml) with LTA (2 mg). The triplet of lines observed [g = 2.0064, $A(^{14}N)$ = 9.0 G] was clearly absent from the mixture above.

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