Reactions of *N*-Nitrenes with Allyl Aryl Sulphides: *N*-Heteroarylsulphenamides

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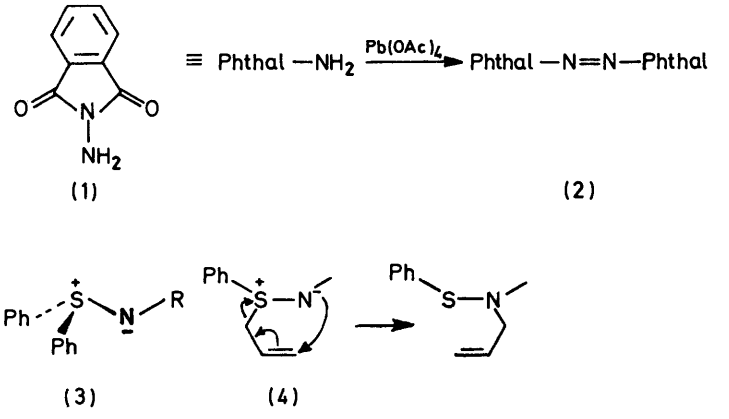
Oxidation of *N*-aminophthalimide, 3-aminobenzoxazol-2(3*H*)-one, and 1-amino-2-quinolone with lead tetra-acetate in the presence of various substituted allyl aryl sulphides gives the corresponding *N*-allyl-*N*-heteroarylsulphenamides by [2,3] sigmatropic rearrangement of the intermediate *N*-heteroarylsulphimides. The n.m.r. spectra of the sulphenamides sometimes show evidence for the presence of diastereoisomers, and a diastereoisomer has been isolated in pure form in one case. An explanation is offered for the widely differing thermal stabilities of these sulphenamides.

THERE is good evidence that oxidation of a variety of *N*-amino-heterocyclic compounds proceeds *via* *N*-nitrenes.[1-3] Evidence from trapping experiments, particularly with olefins, suggests that these nitrenes have singlet ground states.[1,2,4] Other π-electron-containing traps have been used, including acetylenes,[5] allenes,[6] and aromatic compounds.[7] Dimethyl sulphoxide is particularly effective as a trap, especially when used as a solvent for the reaction.[8] In the absence of any efficient trapping agent for the nitrene, this role is often assumed by the parent *N*-amino-heterocycle, with the eventual formation of tetrazenes.[9] Indirect evidence for the trapping of *N*-phthalimidonitrene by sulphides comes from the work of Jones, who has shown that the presence of diphenyl sulphide in the oxidation of *N*-aminophthalimide (1) with lead tetra-acetate changes the stereochemistry of the product, diphthaloyltetrazene (2) from *trans* to *cis*.[10] The sulphimide (3) was postulated as the first-formed intermediate. We reasoned that such a sulphimide might be diverted from further reaction with *N*-phthalimidonitrene and formation of *cis*-tetrazene if an alternative intramolecular reaction was available. An attractive scheme was to incorporate an allyl group as one

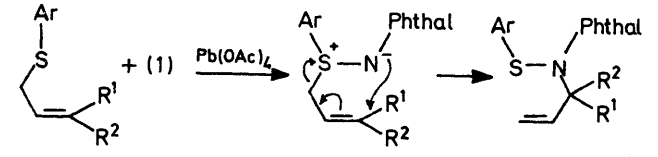


SCHEME 1

[1] R. S. Atkinson and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 772.
[2] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W Rees, *J. Chem. Soc.* (*C*), 1970, 576.
[3] H. Person, C. Fayat, F. Tonnard, and A. Foucaud, *Bull. Soc. chim. France*, 1974, 635; F. Schröppel and J. Sauer, *Tetrahedron Letters*, 1974, 2945; K. K. Mayer, F. Schröppel, and J. Sauer, *ibid.*, 1972, 899; K. Sakai and J.-P. Anselme, *ibid.*, 1970, 3851.
[4] L. J. Hayes, F. P. Billingsley, and C. Trindle, *J. Org. Chem.*, 1972, **37**, 3924; N. C. Baird and R. F. Barr, *Canad. J. Chem.*, 1973, **51**, 3303.
[5] D. J. Anderson, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1973, 550.
[6] R. S. Atkinson and J. R. Malpass, *Tetrahedron Letters*, 1975, 4305.
[7] D. W. Jones, *J.C.S. Perkin I*, 1972, 225, 2728; *J.C.S. Chem. Comm.*, 1973, 67.
[8] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, *J.C.S. Perkin I*, 1972, 1317; S. Colonna and C. J. M. Stirling, *ibid.*, 1974, 2120.
[9] L. Hoesch and A. S. Dreiding, *Helv. Chim. Acta*, 1975, **58**, 980.
[10] D. W. Jones, *Chem. Comm.*, 1970, 1084.

of the sulphide substituents which would allow a [2,3] sigmatropic rearrangement as an intramolecular diversion (Scheme 1). The occurrence of such a rearrangement in allylsulphimides (4) had been experimentally demonstrated by Challenger *et al.*[11] who prepared their allylsulphimides by reaction of substituted allyl aryl sulphides with Chloramine T—a reaction which is not believed to involve a nitrene.[12] In many cases their allylsulphimides were isolable and rearranged on heating or spontaneously.

When *N*-aminophthalimide (1) was oxidised with lead tetra-acetate in methylene chloride containing allyl *p*-chlorophenyl sulphide (5) at room temperature, the



(5) $R^1 = R^2 = H$
(8) $R^1 = H, R^2 = Me$
Ar = *p*-ClC_6H_4 throughout

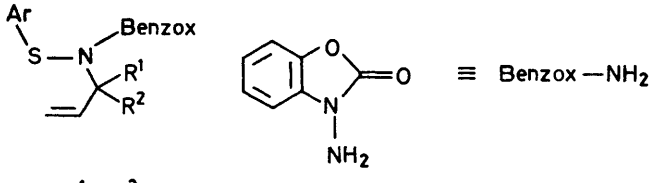
(7)

(6) $R^1 = R^2 = H$
(9) $R^1 = H, R^2 = Me$
(17) $R^1 = R^2 = Me$

two products isolated were the *cis*-tetrazene (2) (9%) and the sulphenamide (6) (61%).[13] The latter product is evidently the result of a [2,3] sigmatropic rearrangement of the sulphimide (7).

A similar oxidation of (1) in the presence of *trans*-but-2-enyl *p*-chlorophenyl sulphide (8), obtained in crystalline form (below room temperature) from the reaction of *p*-chlorobenzenethiolate with *trans*-1-bromobut-2-ene, gave the corresponding sulphenamide (9) (60%) in addition to the *cis*-tetrazene (2) (8%). Analogous sulphenamides (10) (64%) and (11) (54%) were obtained when *N*-aminobenzoxazolone (12) was substituted for *N*-aminophthalimide in these reactions.

Chemical evidence for the sulphenamide structures for (10) and (11) includes the reaction of (11) with *p*-chlorobenzenethiol, which cleaves the sulphur–nitrogen bond [14] to produce the crystalline olefin (13) (55%) and bis-(*p*-chlorophenyl)disulphide (90%). Desulphurisation of



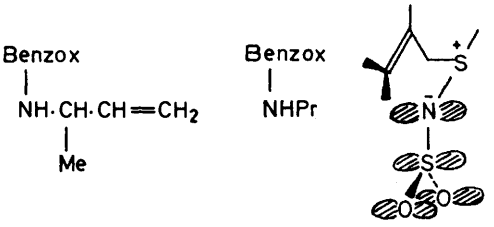
(10) $R^1 = R^2 = H$
(11) $R^1 = H, R^2 = Me$
(18) $R^1 = R^2 = Me$

(12)

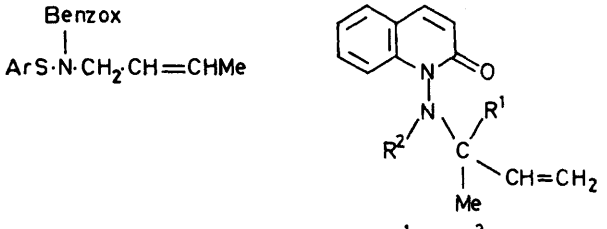
(10) by shaking with Raney nickel in ethyl acetate gave (14) (80%), with saturation of the double bond accompanying desulphurisation.

[11] P. A. Briscoe, F. Challenger, and P. S. Duckworth, *J. Chem. Soc.*, 1956, 1755 and earlier papers.
[12] D. S. Breslow in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 286; F. Ruff and A. Kucsman, *J.C.S. Perkin II*, 1975, 509.

The [2,3] sigmatropic rearrangement of the intermediate sulphimides to sulphenamides reported here evidently occurs more easily than in the cases examined by Challenger *et al.* No evidence for the intermediate sulphimide was obtained when the oxidation of *N*-aminobenzoxazolone (12) was carried out in the presence of the methallyl sulphide (8) at −10 °C and the reaction mixture (after removal of lead diacetate) was examined by n.m.r. without any intermediate warming of the solution. An extension of the explanation of Baldwin [15] can account for the decreased reactivity of Challenger's sulphimides, which all bear a sulphonyl group on the nitrogen atom: resonance delocalisation of the negative charge on the nitrogen into the sulphonyl group must be destroyed at the transition state for the rearrangement (15) whereas no such delocalisation is present in sulphimides such as (7). Also absent from the spectrum of the crude reaction mixture [which contains the sulphenamide (11) and



(13) (14) (15)



(16)

(19) $R^1 = H, R^2 = SAr$
(20) $R^1 = Me, R^2 = SAr$
(22) $R^1 = Me, R^2 = H$

unchanged methallyl sulphide (8)] are signals from (16), a product which would be expected if a radical mechanism for the rearrangement were operating.[15]

Spectroscopic support for the sulphenamide structures (6), (9), (10), and (11), with inversion of the allyl group as required by the [2,3] sigmatropic rearrangement, comes from n.m.r. spectra, particularly that of (11). For this compound, at room temperature, a broadened singlet is observed (δ 1.41 in $CDCl_3$) for the methyl group which separates into two doublets (δ 1.36 and 1.50, *J* 6.5 Hz, ratio 2 : 3) as the temperature is lowered and collapses to a sharp doublet at higher temperatures (T_c *ca.* 27 °C). Such variable temperature behaviour has

[13] Preliminary communication, R. S. Atkinson and S. B. Awad, *J.C.S. Chem. Comm.*, 1975, 651.
[14] A. Fontana, F. Marchiori, L. Moroder, and E. Scoffone, *Tetrahedron Letters*, 1966, 2985; T. Mukaiyama and K. Takahashi, *ibid.*, 1968, 5907.
[15] J. E. Baldwin, J. E. Brown, and R. W. Gordwell, *Chem. Comm.*, 1970, 31.

been previously observed for many other sulphenamides and shown to be the result of accelerated rotation about the S–N bond.[16,17] The chiral axis established at lower temperature means that diastereoisomers are observable by n.m.r. when an additional chiral centre is present as in (11). An alternative explanation for the n.m.r. behaviour involving slow inversion at the sulphenamide nitrogen has been eliminated for examples previously examined.* However, electronegative substituents concontaining unshared electron pairs (O, N, Cl) have been shown to have a retarding effect upon the amine nitrogen inversion rate, and the limited number of amines bearing two such substituents have such grossly retarded inversion rates that separation of diastereoisomers is practicable in suitable cases.[18] Nevertheless, this same retardation may not be shown by sulphur, to judge from the effect of this atom upon the inversion barrier in aziridines where *N*-sulphur substituents lower the barrier relative to *N*-alkyl groups in contrast to *N*-oxygen, *N*-chloro, or *N*-nitrogen substituents (including *N*-benzoxazolone).[19] Assuming that the same effect of sulphur holds in the case of (11), therefore, one would expect an inversion barrier lower than that in an acyclic hydrazine [20] and certainly far lower than the energy barriers in the present case (see later).

In order to exclude slow nitrogen inversion as the phenomenon responsible for the observation of diastereoisomers of (11) by n.m.r. spectroscopy at lower temperatures, we prepared *p*-chlorophenyl dimethylallyl sulphide and the sulphenamides (17) and (18) derived therefrom. For the case of slow nitrogen inversion, the introduction of two methyl groups as in (18) should lower [21] the energy barrier relative to (11) (steric assistance to inversion) as determined from T_c for the two diastereotopic methyl groups, whereas the reverse is to be expected if slow rotation about the S–N bond is responsible. Unfortunately, the signals for the two methyl groups in (18) appear as a sharp singlet, which remains as such down to −50 °C even at 220 MHz. In the ^{13}C n.m.r. spectrum of (18) also, signals for the two methyl groups appear as a singlet down to −50 °C. The two methyl groups in (17) likewise give rise to a singlet, but in any case only one diastereoisomer was observed in the case of (9). We therefore synthesised the sulphenamides (19) and (20), since the 2-quinolone ring is known to have substantial shielding and deshielding effects on methyl groups and protons, respectively, which are located *cis* to it on an aziridine ring.[19] The crystalline sulphenamide (19) shows two methyl doublets (δ 0.93 and 1.48 in $CFCl_3$) whose ratio initially before crystallisation was *ca.* 1 : 2. No coalescence of these two doublets was observable up to 92 °C but the ratio of the two doublets changed significantly at higher temperature, reaching an equilibrium value (5 : 4) after heating at 100 °C for 30 min. Heating at a higher temperature resulted in gradual thermal decomposition, with the methyl doublet ratio retaining the above equilibrium value. For the dimethyl analogue (20) the non-equivalence of the diastereotopic methyl groups was best seen in $CFCl_3$, and no coalescence was observed up to 90 °C.

The absence of coalescence in the case of (19) and the presence of signals for two diastereoisomers in the n.m.r. spectrum led us to attempt the separation of the isomers. By repeated crystallisation from light petroleum, that diastereoisomer having the lower field doublet (present initially in the lesser amount) was removed and the pure diastereoisomer thus obtained, having the higher field doublet, had m.p. 76.5—78 °C. Evidently the barrier to interconversion of the two diastereoisomers in this case is far larger than that obtaining in the case of (21),[22] the only other sulphenamide where such a separation has been achieved. Interconversion of the diastereoisomers in the case of (21) occurs in solution at temperatures below −20 °C.

It is possible that neither slow nitrogen inversion nor slow rotation about the sulphur–nitrogen bond, but slow rotation about the nitrogen–nitrogen (heterocycle) bond is responsible for the observation of diastereoisomers in the case of (19) and (11) and the diastereotopic methyl groups in (20). This explanation accounts for the lack of observation of diastereoisomers in the case of (9), where the symmetry of the phthalimido-group means that there is no chiral axis. The sulphur-free compound (22) also shows diastereotopic methyl groups, with coalescence at *ca.* 20 °C.[23]

An *X*-ray crystal structure determination of the isolated diastereoisomer of (19) is in progress, and may help to decide the nature of the barrier which allows its isolation.

Thermal decomposition of these heterocyclic sulphenamides takes place at significantly different temperatures. Thus the benzoxazolone-substituted compound (11) is converted almost quantitatively into the thio-oxime derivative (23) and benzoxazolone (Scheme 2) on boiling in benzene for 2 h. As previously reported,[24] this decomposition proceeds *via* homolysis of the N–N bond and the two intermediate radicals so generated can both be identified by e.s.r. spectroscopy on heating at 110 °C in chlorobenzene solution.

Thermolysis of the 2-quinolone-sulphenamide (19) yields the same thio-oxime (23), whose appearance can be conveniently monitored by its singlet n.m.r. methyl

* An exception is the case of sulphenamides with the nitrogen as part of an aziridine ring (see ref. 17).

[16] M. Raban, G. W. J. Kenney, and F. B. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 6677; M. Raban and F. B. Jones, *ibid.*, 1971, **93**, 2692.

[17] J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 1298.

[18] K. Muller and A. Eschenmoser, *Helv. Chim. Acta*, 1969, **52**, 1823, and references therein.

[19] D. J. Anderson, D. C. Horwell, and R. S. Atkinson, *J. Chem. Soc.* (*C*), 1971, 624.

[20] M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, 1973, **95**, 1562.

[21] See A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400.

[22] M. Raban and S. K. Lauderback, *J. Amer. Chem. Soc.*, 1971, **93**, 2781.

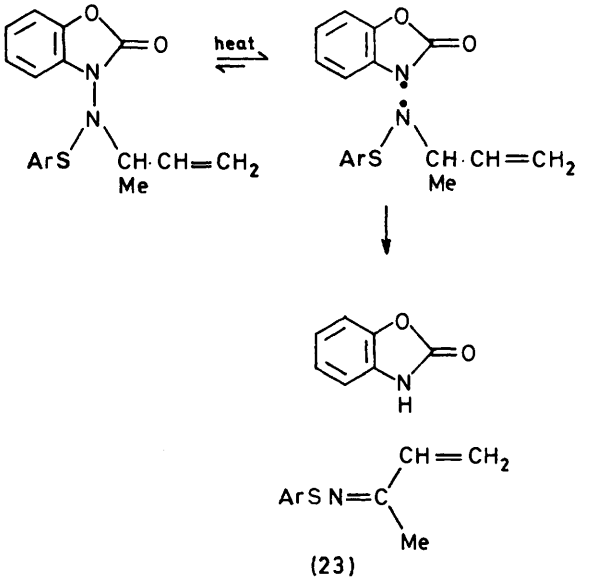
[23] R. S. Atkinson and J. R. Malpass, unpublished work.

[24] R. S. Atkinson, S. B. Awad, E. A. Smith, and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1976, 22.

signal. Decomposition of (19) was only *ca.* 13% complete after heating for 2 h at 100 °C. Thermolysis of the corresponding phthalimido adduct (9) is complicated by the decomposition of the thio-oxime (23) at the temperature required, but even in boiling bromobenzene (156 °C) after 2 h, substantial amounts of starting material remained. Evidently this sulphenamide is significantly more stable than (11) and (19).

A most significant observation was that e.s.r. signals from the benzoxazolone radical in chlorobenzene were observable even at a temperature as low as 48 °C. This suggests that the coalescence observed in the n.m.r. spectrum of this compound may be neither the result of accelerated inversion at nitrogen nor increasingly rapid rotation about the S–N or N–N bond, but interconversion of the two diastereoisomers by homolysis–recombination.

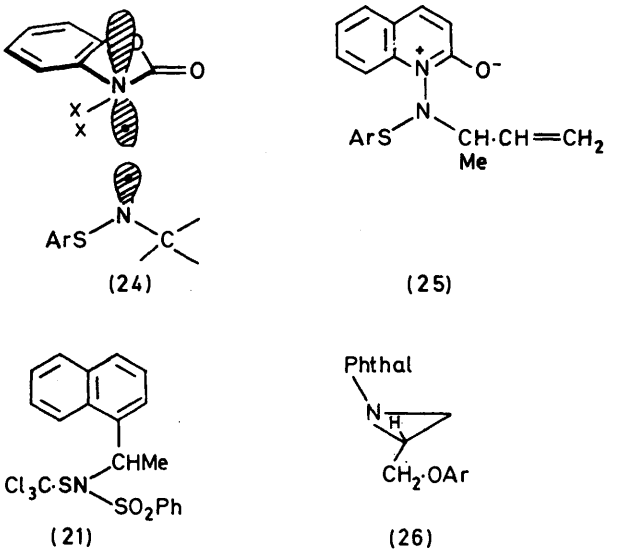
Whatever the process responsible for the n.m.r. behaviour of (11) it is attractive to attribute the order of thermal stability of (11), (19), and (9) in terms of the relative ease of formation of the corresponding heterocyclic radicals. For the case of (11), in particular, an incipient π-radical (24), formed by cleavage of the N–N bond, would be more extensively delocalised than the corresponding phthalimido-radical. Moreover, the necessary N–N σ-bond bending with loss of amide resonance would be expected to be simpler for the case of (11), where compensation from the ring oxygen is available. The greater stability of the 2-quinolone-sulphenamide (19) than of (11) may also be a result of the importance of



SCHEME 2

the resonance contribution (25) to this ring system since this resonance must be destroyed during formation of the π-radical analogous to (24).

The reaction of the *N*-amino-heterocyclic compounds with allyl sulphides and lead tetra-acetate reported here could conceivably proceed *via* reaction of a diacetoxysulphurane (formed from reaction between the sulphide and lead tetra-acetate) with the *N*-amino-heterocycle,



i.e. by-passing formation of the nitrene.[25] We can exclude this mechanism on two counts: (*a*) allyl *p*-chlorophenyl sulphide and lead tetra-acetate are recovered quantitatively from the reaction in the absence of *N*-amino-heterocycle, and (*b*) thermal generation of *N*-phthalimido-nitrene [26] from its 2-acetylbenzofuran adduct in the presence of *p*-chlorophenyl dimethylallyl sulphide gave the sulphenamide (17) in 28% yield.

Attempts to extend the reactions reported here to allyl *p*-chlorophenyl ether were unsuccessful. The only product isolated was the aziridine (26). Significantly, no *cis*-diphthaloyltetrazene (2) was isolated either.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and are corrected. The i.r. spectra of crystalline compounds were determined for Nujol mulls and of other compounds for thin films. N.m.r. spectra were measured with a Varian T60 or JEOL-PS-100 instrument and mass spectra with an A.E.I. MS9 spectrometer. Petroleum refers to the fraction b.p. 60—80°. Basic alumina is Laporte type H, 100—200 mesh. *N*-Aminophthalimide was prepared by the method of Drew and Hatt [27] and 3-aminobenzoxazol-2(3*H*)-one by the method previously reported.[2]

trans-*But-2-enyl* p-*Chlorophenyl Sulphide* (8).—This was prepared from equimolecular quantities of sodium *p*-chlorobenzenethiolate and *trans*-but-2-enyl bromide by the literature method for the preparation of allyl *p*-chlorophenyl sulphide.[28] It was purified by dissolving in light petroleum, cooling in an ice–salt bath, and filtering off rapidly the crystals obtained (m.p. below room temperature) (yield 85%); δ(CCl_4) 7.0 (s, 4 × ArH), 5.5—5.2 (m, 2 × olefinic H), 3.5—3.15 (m, CH_2), and 1.7—1.5 (m, CH_3).

p-*Chlorophenyl 2-Methylbut-2-enyl Sulphide.*—This was similarly prepared from 2-methylbut-2-enyl chloride and sodium *p*-chlorobenzenethiolate. It also crystallised from light petroleum at low temperature (m.p. below room

[25] J. I. G. Cadogan and I. Gosney, *J.C.S. Perkin I*, 1974, 466.
[26] D. W. Jones, *J.C.S. Chem. Comm.*, 1972, 884.
[27] H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 1937, 16.
[28] A. M. Kuliev, E. N. Usbora, Yu. M. Sultanov, and A. B. Kuliev, *Zhur. org. Khim.*, 1967, **3**, 1247.

temperature); yield 87%; δ(CCl_4) 7.0br (s, 4 × ArH), 5.15 [t (further split), *J* 7.5 Hz, H-3], 3.36 (d, *J* 7.5 Hz, CH_2), and 1.65 and 1.53 (2 × s, 2 × CH_3).

Reactions of Nitrenes with Allyl Sulphide Derivatives.—General procedure. The *N*-amino-compound (0.004 mol) was stirred in dry dichloromethane (10 ml) and the allyl sulphide (0.005 mol) was added. Lead tetra-acetate (0.004 mol) was added to the stirred suspension at room temperature over *ca.* 5 min. After a further 15 min the mixture was filtered, the residual solid was washed with dichloromethane, and the combined filtrate and washings were concentrated at room temperature under reduced pressure. In the reaction with *N*-aminophthalimide, addition of a little light petroleum gave a solid which crystallised from benzene to give *cis*-diphthaloyltetrazene, m.p. 160° (decomp.), identical with sample prepared by oxidation of *N*-aminophthalimide in the presence of diphenyl sulphide.[10] Chromatography of the mother liquor on basic alumina [light petroleum–ethyl acetate (5 : 1) as eluant] gave the corresponding *N*-heteroarylsulphenamides after elution of unchanged allyl sulphide. The following compounds were obtained in this way: N-*allyl*-N-*phthalimido*-p-*chlorobenzenesulphenamide* (6) from *N*-aminophthalimide and allyl *p*-chlorophenyl sulphide as crystals (from light petroleum), m.p. 109° (61%) (Found: C, 58.95; H, 3.4; N, 8.2. $C_{17}H_{13}ClN_2O_2S$ requires C, 59.2; H, 3.75; N, 8.15%); δ($CDCl_3$) 7.62 (s, 4 × phthalimido H), 7.26 (AA'BB', *p*-ClC_6H_4), 6.15—5.55 and 5.3—4.85 (structured m, 3 × olefinic H), and 4.15 (d, *J* 6.5 Hz, CH_2); *m/e* 346/344 (M^+), 305, 303, 201, 198, 196, 148, 147, 146, 144, 130, and 104; $\nu_{max.}$ 1 787m, 1 727br, 1 190m, 1 090m, 1 010s, 987s, 941s, 880s, 849s, 819s, and 711s cm^{-1}; N-(1-*methylallyl*)-N-*phthalimido*-p-*chlorobenzenesulphenamide* (9) from *N*-aminophthalimide and *trans*-but-2-enyl *p*-chlorophenyl sulphide as crystals (from methanol), m.p. 72—73° (60%) (Found: C, 60.15; H, 4.2; N, 7.75. $C_{18}H_{15}ClN_2O_2S$ requires C, 60.25; H, 4.2; N, 7.8%); δ($CDCl_3$) 7.66br (s, 4 × phthalimido H), 7.32 (AA'BB', *p*-ClC_6H_4), 6.15—5.45 and 5.25—4.75 (structured m, 3 × olefinic H), 4.6—4.0 (m, CH_3·C*H*), and 1.35 (d, *J* 7 Hz, CH_3); *m/e* 360/358 (M^+), 305, 303, 288, 286, 278, 276, 213, 211, 201, 162, 148, 147, 146, 130, 104, 76, and 70; $\nu_{max.}$ 1 784m, 1 733br, 1 190m, 1 088, 1 007s, 998s, 990m, 945s, 878s, 814s, and 708s cm^{-1} (no conclusive evidence for diastereoisomers was shown by the n.m.r. spectrum of this compound); N-(1,1-*dimethylallyl*)-N-*phthalimido*-p-*chlorobenzenesulphenamide* (17) from *N*-aminophthalimide and *p*-chlorophenyl 2-methylbut-2-enyl sulphide as crystals (from light petroleum), m.p. 112—114° (64%) (Found: C, 61.35; H, 4.6; N, 7.5. $C_{19}H_{17}ClN_2O_2S$ requires C, 61.2; H, 4.55; N, 7.5%); δ($CDCl_3$) 7.57br (s, 4 × phthalimido H), 7.23 (AA'BB', *p*ClC_6H_4), 6.06 (dd, *J* 16.5 × 10 Hz, :CH), 5.0 and 4.93 (2 overlapping d, *J* 16.5 and 10 Hz, CH_2), and 1.43 (s, 2 × CH_3); *m/e* 374/372 (M^+), 306, 305, 304, 303, 278, 276, 162, 161, 148, 147, 146, 144 104, and 88; $\nu_{max.}$ 1 786m, 1 726br, 1 192m, 1 143m, 1 090s, 1 005s, 996s, 936m, 923m, 877s, 818s, 780m, 736m, and 710s cm^{-1} [this compound was also obtained by heating a mixture of the 2-acetylbenzofuran–phthalimidonitrene adduct[25] (0.4 g) and *p*-chlorophenyl 2-methylbut-2-enyl sulphide (0.7 g) in boiling benzene (10 ml) for 5 h; it separated from light petroleum (0.13 g, 28%) as crystals identical with a sample prepared by the general procedure above]; N-*allyl*-N-(2,3-*dihydro*-2-*oxobenzoxazol*-3-*yl*)-p-*chlorobenzenesulphenamide* (10) from *N*-aminobenzoxazol-2(3*H*)-one and allyl *p*-chlorophenyl sulphide as crystals (from light petroleum), m.p. 97° (64%) (Found: C, 57.8; H, 4.05; N, 8.4. $C_{16}H_{13}ClN_2O_2S$ requires C, 57.75; H, 3.9; N, 8.4%); δ($CDCl_3$) 7.55—6.75 (m, 8 × ArH), 6.45—5.55 and 5.4—4.95 (m, 3 × olefinic H), and 4.27 (d, *J* 6.5 Hz, CH_2); *m/e* 334/332 (M^+), 288, 286, 198, 196, 188, 146, 144, and 135; $\nu_{max.}$ 1 773br, 1 247m, 1 114m, 1 087m, 1 012s, 983m, 934s, 868m, 820m, 810m, 748s, 735s, and 726s cm^{-1}; N-(1,2-*dihydro*-2-*oxoquinolin*-1-*yl*)-N-(1-*methylallyl*)-p-*chlorobenzenesulphenamide* (19) from 1-amino-2-quinolone and *trans*-but-2-enyl *p*-chlorophenyl sulphide as crystals (from light petroleum), m.p. 57—59 °C (58%) (Found: C, 63.9; H, 4.7; N, 7.9. $C_{19}H_{17}ClN_2OS$ requires C, 63.95; H, 4.8; N, 7.85%); δ($CFCl_3$; 100 MHz) 7.8—6.9 (m, 8 × ArH and quinoline H-4), 6.55 (d, *J* 9 Hz, quinoline H-3), 6.50 (d, *J* 9 Hz, quinoline H-3), 6.2—5.8 (m, :CH), 5.5—5.0 (m, CH_2), 5.0—4.6 (m, C*H*·CH_3), 1.48 (d, *J* 6.5 Hz, CH_3), and 0.93 (d, *J* 6.5 Hz, CH_3) (two diastereoisomers were present as indicated by the duplicate peaks at δ 6.55, 6.50, 1.48, and 0.93; from integration of peaks at 1.48 and 0.93, respectively, the ratio before crystallisation was *ca.* 1 : 2, and was changed to 5 : 4 after heating in $CFCl_3$ at 100 °C for ½ h; after crystallisation six times from light petroleum, the sample obtained, m.p. 76.5—78°, did not show the signals at δ 6.50 and 1.48); *m/e* 358/356 (M^+), 303, 301, 288, 286, 213, 211, 159, 146, 144, 143, 117, and 108; $\nu_{max.}$ 1 654s,br, 1 596m, and 1 559m cm^{-1}; N-(1,2-*dihydro*-2-*oxoquinolin*-1-*yl*)-N-(1,1-*dimethylallyl*)-p-*chlorobenzenesulphenamide* (20) from 1-amino-2-quinolone and 2-methylbut-2-enyl *p*-chlorophenyl sulphide as crystals (from light petroleum), m.p. 81—82° (64%) (Found: C, 64.9; H, 5.15; N, 7.6. $C_{20}H_{19}ClN_2OS$ requires C, 64.75; H, 5.1; N, 7.55%); δ($CDCl_3$; 100 MHz) 7.9—7.1 (m, 8 × ArH and quinoline H-4), 6.80 (d, *J* 9 Hz, quinoline H-3), 6.34 (d × d, *J* 17 and 11 Hz, :CH), 5.20 (d, *J* 17 Hz, *trans*-*H*CH), 5.09 (d, *J* 11 Hz, *cis*-HC*H*), and 1.48 and 1.42 (2 s, 2 × CH_3) (in $CFCl_3$ both signals for the diastereotopic methyl groups were visible at 90 °C); *m/e* 372/370 (M^+), 227, 161, 160, 159, 145, 144, 143, and 109; $\nu_{max.}$ 1 657s, 1 599m, and 1 563m cm^{-1}; N-(2,3-*dihydro*-2-*oxobenzoxazol*-3-*yl*)-N-(1-*methylallyl*)-p-*chlorobenzenesulphenamide* (11) from *N*-aminobenzoxazol-2(3*H*)-one and *trans*-but-2-enyl *p*-chlorophenyl sulphide as crystals (from light petroleum), m.p. 74° (54%) (Found: C, 58.7; H, 4.4; N, 8.15. $C_{17}H_{15}ClN_2O_2S$ requires C, 58.85; H, 4.35; N, 8.1%); δ($CDCl_3$; 100 MHz) 7.41 (AA'BB', *p*-ClC_6H_4), 7.13br (s, 4 × benzoxazole H), 6.1—5.45 and 5.38—4.9 (m, CH_2:CH), 2.7—2.22 (m, CH_3C*H*), and 1.6—1.2br (s, CH_3) (at −54 °C this CH_3 signal separated into two doublets, δ 1.36 and 1.50, *J* 6.5 Hz, ratio 2 : 3, and at +59 °C collapsed to a sharp doublet, *J* 6.5 Hz); *m/e* 348/346 (M^+), 288, 286, 213, 211, 146, 144, and 135; $\nu_{max.}$ 1 770br, 1 251s, 1 091m, 1 012m, 1 008m, 820m, 749s, and 738m cm^{-1}; N-(2,3-*dihydro*-2-*oxobenzoxazol*-3-*yl*)-N-(1,1-*dimethylallyl*)-p-*chlorobenzenesulphenamide* (18) from *N*-aminobenzoxazol-2(3*H*)-one and 2-methylbut-2-enyl *p*-chlorophenyl sulphide as crystals (from light petroleum), m.p. 116—117° (60%) (Found: C, 59.75; H, 4.8; N, 7.8. $C_{18}H_{17}ClN_2O_2S$ requires C, 59.9; H, 4.7; N, 7.75%); δ(CCl_4) 7.15 (AA'BB', *p*-ClC_6H_4) superimposed on 7.26—6.8 (m, 4 × benzoxazole H), 6.08 (dd, *J* 16.5 × 10 Hz, :CH), 5.03 and 4.96 (2 overlapping d, *J* 16.5 and 10 Hz, :CH_2), and 1.46 (s, 2 × CH_3); *m/e* 362/360 (M^+), 288, 287, 286, 229, 227, 212, 211, 210, 161, 159, 146, 145, 144, 143, 135, 110, 109, 108, 91, and 79; $\nu_{max.}$ 1 770br, 1 258m, 1 095s, 1 021s, 1 011s, 935m, 881m, 826m, 752s, and 735m cm^{-1}.

Reaction of N-*Phthalimidonitrene with Allyl* p-*Chlorophenyl Ether*—Lead tetra-acetate (1.17 g) was added in small portions over 5 min to a stirred mixture of *N*-amino-

phthalimide (0.64 g) and allyl *p*-chlorophenyl ether (1.68 g) in dichloromethane (10 ml). The mixture was stirred for 30 min and the lead diacetate formed was filtered off. The filtrate was diluted with light petroleum to give a solid (0.32 g) and the residual mother liquor was concentrated and chromatographed on basic alumina [ethyl acetate–light petroleum (1 : 5)]. After elution of unchanged allyl ether (1 g), 2-(p-*chlorophenoxymethyl*)-1-*phthalimidoaziridine* (26) (10%) was eluted; m.p. 135° (from chloroform–light petroleum) (Found: C, 61.85; H, 3.9; N, 8.55. $C_{17}H_{13}ClN_2O_3$ requires C, 62.1; H, 3.95; N, 8.5%); δ($CDCl_3$) 7.55 (s, 4 × phthalimido H), 6.93—6.5 (AA'BB', *p*-ClC_6H_4), 4.30 and 3.95 [2 × dd (ABX), *J* 10 and 4.5 Hz, CH_2·O], and 3.1—2.65 and 2.63—2.35 (structured m, 3 × aziridine H); $\nu_{max.}$ 1 787w, 1 772w, 1 711br, 1 494s, 1 291m, 1 252s, 1 216m, 1 174s, 1 164s, 1 135m, 1 035s, 970s, 893s, 819s, and 707s cm^{-1}.

The solid (0.32 g) separated above appeared (i.r.) to be a mixture of *trans*-diphthaloyltetrazene and phthalimide. No *cis*-diphthaloyltetrazene was isolated, although the presence of small amounts of the latter in the mixture cannot be excluded.

Reaction of the Sulphenamide (11) *with* p-*Chlorobenzenethiol*.—A mixture of the sulphenamide (11) (0.2 g) and *p*-chlorobenzenethiol (0.2 g) was heated under reflux in carbon tetrachloride for 30 min. The solution was cooled and diluted with light petroleum to give benzoxazol-2(3*H*)-one (20 mg). The combined solutions were evaporated and the residue crystallised from light petroleum to give bis-(*p*-chlorophenyl) disulphide, m.p. and mixed m.p. 71°. Chromatography of the mother liquor on basic alumina (light petroleum) gave more of this disulphide (total 90%); ethyl acetate then eluted N-(1-*methylallylamino*)*benzoxazol*-2(3H)-*one* (13), m.p. 65—66° (from light petroleum) (Found: C, 64.45; H, 6.0; N, 13.55. $C_{11}H_{12}N_2O_2$ requires C, 64.7; H, 5.9; N, 13.75%); δ(CCl_4) 6.92 (s, 4 × ArH), 6.0—4.8 (m, 3 × olefinic H), 4.6—4.3br (s, NH), 4.2—3.7 (m, CH), and 1.2 (d, *J* 5.5 Hz, CH_3); *m/e* 204 (M^+), 150, 149, 135, 134, 105, 79, 78, 70, and 55; $\nu_{max.}$ 3 288s, 1 788s, 1 750br, 1 411m, 1 261m, 1 114m,br, 1 089s, 1 010s, 941m, and 745s cm^{-1}.

Desulphurisation of the Sulphenamide (10).—A mixture of compound (10) (0.2 g) and Raney nickel (*ca.* 5 g) in ethyl acetate (10 ml) was shaken for 24 h. The solution was decanted, filtered, and evaporated. Distillation of the oily residue under vacuum gave N-*propylaminobenzoxazol*-2(3H)-*one* (14) (85 mg) (Found: C, 62.4; H, 6.4; N, 14.65. $C_{10}H_{12}N_2O_2$ requires C, 62.5; H, 6.25; N, 14.6%); δ(CCl_4) 6.98 (s, 4 × ArH), 4.78 (t, *J* 5.5 Hz, NH), 3.08 [4 lines (further split), N·CH_2], and 1.9—0.8 (structure dm, CH_2CH_3), $\nu_{max.}$ 3 292w, 1 776br, 1 477s, 1 253s, 1 107m, 1 007m, and 748 cm^{-1}.

Thermal Decomposition of the Sulphenamide (11).—A solution of the sulphenamide (11) (0.5 g) in benzene (10 ml) was heated under reflux for 2 h. The n.m.r. spectrum of the solution showed complete disappearance of the starting material. Benzene was evaporated off and the residue triturated with light petroleum to give benzoxazol-2(3*H*)-one (185 mg), m.p. 168—169°, identical with authentic material. The light petroleum filtrate was evaporated to give an oil which was purified by chromatography on basic alumina (light petroleum). It was identified as the thio-oxime (23) (0.28 g), δ(CCl_4) 7.3—6.8 (m, 4 × ArH), 6.3 (dd, *J* 16 and 10 Hz, :CH), 5.33 (d, *J* 16 Hz, *trans*-*H*CH:), 5.26 (d, *J* 10 Hz, *cis*-HC*H*:), and 2.06 (s, CH_3) [also invariably present was a small singlet, δ 2.20, which could be the minor isomer (*syn–anti* with respect to the C=N); ratio δ 2.20 to δ 2.06 *ca.* 1 : 7]; $\nu_{max.}$ 1 610w, 1 568w, 1 476s, 1 390s, 1 364m, 1 106m, 1 090s, 1 010s, 990m, 927m, 811s, 742s and 730m cm^{-1}. This compound decomposed upon attempted distillation under reduced pressure.

Thermal decomposition of (19) was carried out similarly by heating in chlorotrifluoromethane (sealed tube) for 2 h at 130 °C, giving 2-quinolone and the same thio-oxime (23) in nearly quantitative yield.

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