N-(Heterocyclic)sulphenamides by [2,3] Sigmatropic Rearrangement of Sulphilimines

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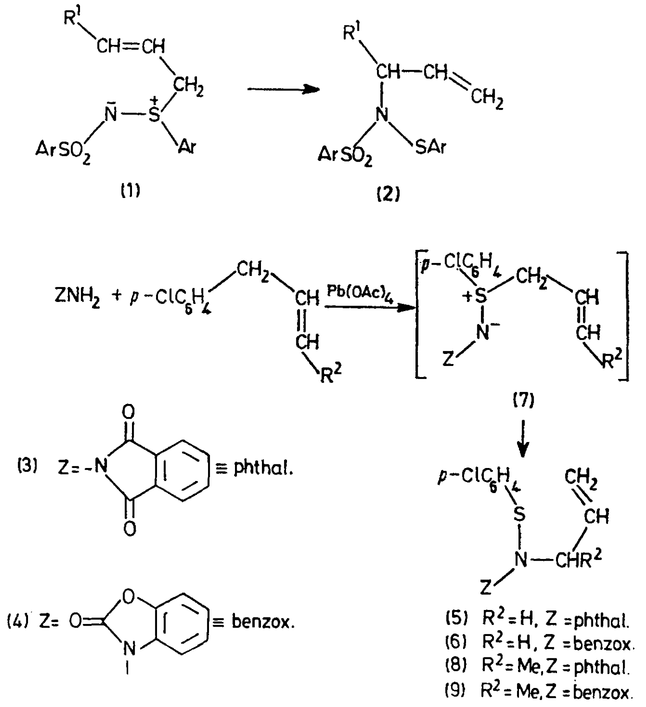
Summary Addition of *N*-nitrenes to allyl aryl sulphides gives *N*-(heterocyclic)sulphenamides by [2,3]sigmatropic rearrangement of the initially formed sulphilimines.

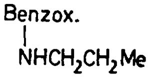
REACTION of chloramine T with allyl aryl sulphides gives sulphilimines (**1**) whose rearrangement to sulphenamides (**2**) was described earlier by Challenger *et al.*[1] and subsequently recognised[2] as one of a number of related [2,3] sigmatropic rearrangements. There is little evidence that a nitrene intermediate is formed from chloramine T in the above reactions[3] but we have now obtained *N*-(heterocyclic) sulphenamides by addition of *N*-nitrenes from (**3**) and (**4**)[4] to allyl aryl sulphides. Thus, oxidation of (**3**) and (**4**) with lead tetra-acetate in CH_2Cl_2 in the presence of allyl *p*-chlorophenyl sulphide gave (**5**), m.p. 109 °C (61%), and (**6**), m.p. 97 °C (64%) respectively, after chromatography over alumina.†



(5) R^2=H, Z =phthal.
(6) R^2=H, Z =benzox.
(8) R^2=Me, Z =phthal.
(9) R^2=Me, Z =benzox.

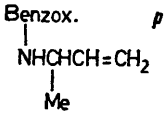
Inversion of the allyl group required by [2,3] sigmatropic rearrangement of an initially formed sulphilimine (**7**)[5] was demonstrated using *trans*-but-2-enyl *p*-chlorophenyl sulphide when (**8**), m.p. 72–73 °C (60%), and (**9**), m.p. 74 °C (54%), *m/e* 346 and 348 (M^+), were obtained from (**3**) and (**4**) respectively. The n.m.r. spectrum of (**9**) strongly supports the sulphenamide structure: at 100 MHz and 25 °C, the methyl group appears as a broadened singlet (δ 1·41, $CDCl_3$) but 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 temperature (T_c *ca.* 27°). Similar behaviour has been noted previously for sulphenamides and shown[6] to be the result of slow rotation about the S–N bond on the n.m.r. time-scale.‡

Reduction of (**6**) with Raney nickel gave (**10**) where saturation of the olefinic bond has accompanied desulphurisation. Reaction of (**9**) with *p*-chlorobenzenethiol in CCl_4 yielded the olefin (**11**), m.p. 65—66 °C (55%), and di-(*p*-chlorophenyl) disulphide (90%), a breakdown characteristic of sulphenamides.[7] Compounds (**5**), (**6**), (**8**), and (**9**) are unusual in having formally only σ-bonds linking the three adjacent heteroatoms. This fact may account for the thermal instability of *e.g.* (**9**) which is converted into 3*H*-benzoxazolin-2-one and the thio-oxime derivative (**12**) in boiling benzene after 2 h.



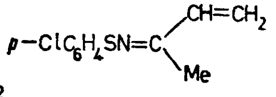
$\text{Benzox.}-NHCH_2CH_2Me$

(10)



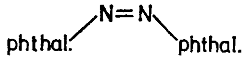
$\text{Benzox.}-NHCH(Me)CH{=}CH_2$

(11)



$p\text{-}ClC_6H_4SN{=}C(CH{=}CH_2)Me$

(12)



phthal.–N=N–phthal.

(13)

Sulphilimines have been proposed as intermediates in the formation of the *cis*-diphthaloyl tetrazene (**13**), when *N*-aminophthalimide is oxidised in the presence of diphenyl sulphide.[8] Our results support this proposal since an isolable by-product from reactions which give (**5**) and (**8**) is the *cis*-tetrazene (**13**) identical with a sample prepared by the literature method.

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† Omission of (**3**) or (**4**) in these experiments leads to a quantitative recovery of lead tetra-acetate and allyl *p*-chlorophenyl sulphide, indicating that the products do not arise by reaction of the *N*-amino-compounds with a sulphurane produced from the sulphide and lead tetra-acetate.

‡ That slow S–N bond rotation (and not slow nitrogen inversion) is responsible for the n.m.r. behaviour in the present case has not yet been proved but the heterocyclic group is certain to raise the inversion barrier at the sulphenamide nitrogen compared to previous acyclic examples studied (see ref. 6, and R. S. Atkinson, *Chem. Comm.*, 1968, 676).

[1] P. A. Briscoe, F. Challenger, and P. S. Duckworth, *J. Chem. Soc.*, 1956, 1755; and earlier papers.

[2] J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Comm.*, 1968, 538.

[3] D. S. Breslow in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 286.

[4] R. S. Atkinson and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 772; D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *ibid.*, 1970, 576.

[5] A stable sulphilimine is obtained in the reaction of ethoxycarbonylnitrene with dimethyl sulphide; M. Okahara and D. Swern, *Tetrahedron Letters*, 1969, 3301.

[6] 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; M. Raban and S. K. Lauderback, *ibid.*, p. 2781; J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 1298.

[7] A. Fontana, F. Marchiori, L. Moroder, and E. Scoffone, *Tetrahedron Letters*, 1966, 2985; T. Mukaiyama and K. Takahashi, *ibid.*, 1968, 5907.

[8] D. W. Jones, *Chem. Comm.*, 1970, 1084.

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