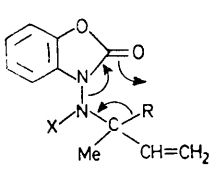
Thermal Decomposition of *N*-Alkenyl-*N*-(2,3-dihydro-2-oxobenzoxazol-3-yl) *S*-*p*-chlorophenylsulphenamides

By ROBERT S. ATKINSON,* SAMI BASSILI AWAD, EDWARD A. SMITH, and MARTYN C. R. SYMONS
(*Department of Chemistry, University of Leicester, Leicester* LE1 7RH)

Summary Thermal decomposition of the title compounds in boiling benzene proceeds by homolysis of the N–N bond, the radicals generated being identified by e.s.r. spectroscopy.

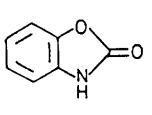
WE have recently reported that thermal decomposition of the sulphenamide (**1**) in boiling benzene for 2 h gives benzoxazole-2(3*H*)-one (**2**) and the thio-oxime derivative (**3**).[1] The low thermal stability of (**1**) was surprising since



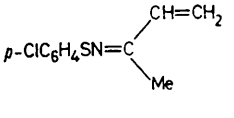
(1) R = H, X = SC_6H_4Cl-*p*

(2) R = H, X = H

(5) R = Me, X = SC_6H_4Cl-*p*

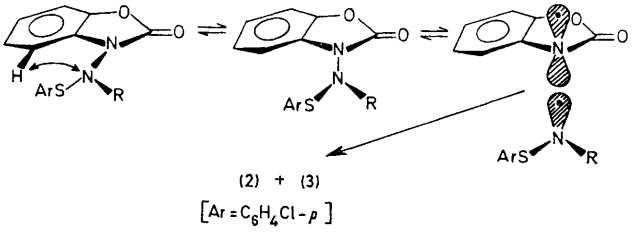


(2)



(3)

the corresponding N–H compound (**4**) was recovered unchanged after heating in boiling xylene for 2 h. Thus a concerted cyclic elimination of (**2**) [retro-ene reaction: arrows in (**1**)] seemed unlikely since the influence of substituents on the rate would be expected to be small. A rate-determining heterolytic cleavage of the N–N bond was also unlikely since the disappearance of the sulphenamide was only *ca.* twice as fast in boiling MeCN as in boiling benzene when monitored by n.m.r. spectroscopy.



(2) + (3)

[Ar = C_6H_4Cl-*p*]

FIGURE

Our observation of e.s.r. signals as (**1**) is heated in PhCl (probe temp. 105 °C) shows that decomposition involves a homolytic cleavage of the N–N bond. Both radical species are observable; the benzoxazolone radical has a set of closely spaced narrow lines with A values of *ca.* 4·3 (4-H), 3·0 (6-H), 0·8 (5-H, 7-H), and 5·9 (^{14}N) G (G = 10^{-4}T).

Comparison with the phenylimino radical[2] PhṄH suggests that delocalisation on to the carbonyl oxygen is significant, probably because an aromatic benzoxazole ring is thereby preserved. For the thioimino radical, four lines are observed with intensities in the ratio 1:2:2:1, giving values of 11 (^{14}N) and 11 (H) G. The small positive g-shift (g_{av} = 2·0073) is evidence for delocalisation of the spin on to the adjacent sulphur.[3]

Support for these assignments comes from thermolysis of the dimethyl analogue (**5**), where a 1:1:1 triplet (A = 11 G) for the now more stable thioimino radical† almost conceals the corresponding multiplets from the benzoxazolone radical.

In contrast to (**1**), the phthalimido-analogue (**1**; phthalimido replacing benzoxazolone) was considerably more stable and, even after boiling in PhBr (156 °C) for 2 h, 50% of the starting material was still present (from n.m.r. spectroscopy).

We suggest that to facilitate radical cleavage of the N–N bond in these sulphenamides, this bond must be bent out of the plane containing the heterocycle. The incipient π-radical can then be extensively delocalised, thus lowering the transition state energy for bond breaking (Figure). This bending of the N–N bond with concomitant loss of the amide resonance energy is less serious for (**1**) where compensation from the adjacent ring oxygen atom is available. Moreover, such bending also relieves a *peri*-interaction with 4-H in the case of (**1**). The phthalimido-π-radical itself also would be less extensively delocalised than the benzoxazolone radical and for this reason would be less easily generated.

In the previously reported n.m.r. spectrum of (**1**), coalescence of the two methyl doublets (T_c *ca.* 27 °C) was assumed to be the result of fast S–N bond rotation on the n.m.r. time-scale. Our observation of strong e.s.r. signals from the benzoxazolone radical on heating (**1**) to only 48 °C suggests that the coalescence observed is more likely the result of accelerated homolysis and re-formation of the N–N bond interconverting the two diastereoisomers present.‡

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† This species is converted into a more stable, as yet unidentified radical which persists in solution at room temperature for several days.

‡ The n.m.r. spectrum of the *N*-quinolin-2-one analogue of (**1**; quinolin-2-one replacing benzoxazolone) shows no coalescence of the corresponding two methyl doublets even at 80 °C and the compound is significantly more stable to heat compared to (**1**).

[1] R. S. Atkinson and S. B. Awad, *J.C.S. Chem. Comm.*, 1975, **651**.
[2] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.
[3] α-Sulphur exerts a strong stabilising influence on carbon radicals, see A. Ohno and Y. Ohnishi, *Tetrahedron Letters*, 1969, 4405; I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.