Oxidation of 2,4-Dinitrobenzenesulphenamide in the Presence of Alkenes: Formation of Aziridines

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Summary Oxidation of 2,4-dinitrobenzenesulphenamide in the presence of electron-rich alkenes yields *N*-2,4-dinitrophenylthioaziridines which have been converted into the corresponding N–H aziridines by reduction.

FLUORO[1]- and chloro-thiazyne[2] F–S≡N and Cl–S≡N are known to trimerise readily. In the limited number of reactions of these compounds which have been examined, their sulphenylnitrene character F–S–$\ddot{\text{N}}$: or Cl–S–$\ddot{\text{N}}$: has not been in evidence. However, reaction of fluorothiazyne with perfluoropropene in the presence of CsF does not give the expected thiazyne (**1**) but secondary products whose formation has been ascribed to the nitrene-like reactivity of (**1**).[3]

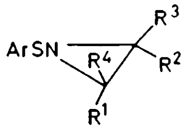
$$(CF_3)_2CFS{\equiv}N \longleftrightarrow (CF_3)_2CFS{-}N$$

(**1**)

We here report that oxidation of 2,4-dinitrobenzenesulphenamide (**2**) in the presence of electron-rich alkenes gives aziridines. Thus oxidation of (**2**) with lead tetra-acetate in dichloromethane containing *trans*-propenylbenzene gave (**3**) (64%), m.p. 115—117 °C, ^{1}H n.m.r. δ(CDCl$_3$) 8·95 (d, *J* 2·5 Hz, ArH-3), 8·45 (d, *J* 8·5 Hz, ArH-6), 8·25 (dd, *J* 2·5 and 8·5 Hz, ArH-5), 7·25 (br s, 5 × ArH), 3·00 (d, *J* 3·5 Hz, aziridine H-3), 2·85 (dq, *J* 3·5 and 5·5 Hz, aziridine H-2), and 1·6 (d, *J* 5·5 Hz, Me).

$ArSNH_2$

(2)



(3) R^1=Ph, R^3=Me, R^2=R^4=H

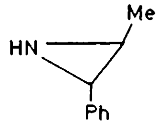
(4) R^1=Ph, R^2=R^3=R^4=H

(5) R^1=Ph, R^4=Me, R^2=R^3=H

(6) R^1=R^3=Me, R^2=R^4=H

(7) R^1=CH=CH$_2$, R^2=R^3=R^4=H

Ar = 2,4-dinitrophenyl

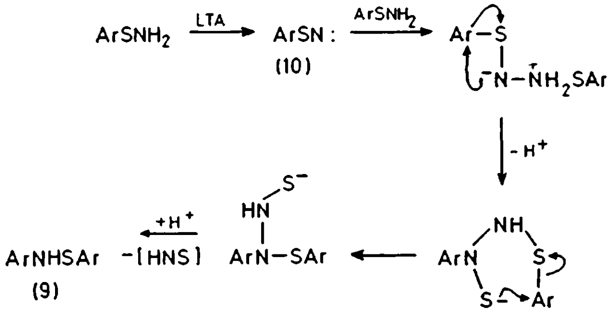


(8)

Likewise, the aziridines (**4**), 38%, m.p. 110—112 °C; (**5**), 61%, oil, and (**6**) 38%, m.p. 132—135 °C were obtained using styrene, α-methylstyrene, and *trans*-but-2-ene respectively. With butadiene, only the product (**7**) from 1,2-addition was isolated in 58% yield, m.p. 113—115 °C, ^{1}H n.m.r. (CDCl$_3$) 9·1 (d, *J* 1·5 Hz, ArH-3), 8·4 (d, *J* 1·5 Hz, ArH-5 and ArH-6), 5·9—5·2 (m, 3 × olefinic H), 2·70 (ddd, *J* 6·8, 6·8, and 3·7 Hz, aziridine H-2), 2·40 (d, *J* 3·7 Hz, aziridine H-3 *cis* to vinyl), and 2·38 (d, *J* 6·8 Hz, aziridine H-3 *trans* to vinyl).

The weakness of the N–S bond allows its cleavage in these sulphenylated aziridines without concomitant ring-opening. Thus reduction of (**3**) with sodium borohydride in ethanol–dichloromethane gave the N–H aziridine (**8**) in 56% yield. It may be that (**2**) can be advantageously used in the conversion of an electron-rich alkene into the corresponding aziridine.

Oxidation of (**2**) in the absence of alkenes gave a yellow crystalline solid, m.p. 231 °C (decomp.), yield 41%, identified as *N*-(2,4-dinitrophenyl)-2,4-dinitrobenzenesulphenamide (**9**), by synthesis from 2,4-dinitroaniline and 2,4-dinitrobenzenesulphenyl chloride. We suggest that (**9**) is formed by attack of 2,4-dinitrobenzenesulphenylnitrene (**10**)[4] on (**2**) followed by two consecutive Smiles rearrangements (Scheme).†



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

No aziridines were isolated from the oxidation of 4-nitro- or 4-chloro-benzenesulphenamides in the presence of styrene; the only products isolated were the corresponding disulphides in 33 and 75% yields respectively. Aziridines were obtained, however, from the oxidation of 2-nitrobenzenesulphenamide in the presence of styrenes.

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† Alternatively, attack of the nitrene (**10**) on the sulphur atom of (**2**) would require only a single Smiles/Stevens rearrangement.

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[3] W. Bludssus, R. Mews, and O. Glemser, *Israel J. Chem.*, 1978, **17**, 137.

[4] R. S. Atkinson and B. D. Judkins, following communication.