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

By ROBERT S. ATKINSON and BRIAN D. JUDKINS (Department of Chemistry, Leicester University, Leicester LE1 7RH)

Summary Oxidation of 2,4-dinitrobenzenesulphenamide in the presence of electron-rich alkenes yields N-2,4dinitrophenylthioaziridines which have been converted into the corresponding N-H aziridines by reduction. FLUORO¹- and chloro-thiazyne² 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-N: or Cl-S-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

$$(CF_3)_2 CFS \equiv N \iff (CF_3)_2 CFS - N$$
(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 tetraacetate in dichloromethane containing trans-propenylbenzene gave (3) (64%), m.p. 115-117 °C, ¹H n.m.r. $\delta(\text{CDCl}_3)$ 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 \times 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).



Ar = 2,4- dinitrophenyl

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 1,2addition was isolated in 58% yield, m.p. 113-115 °C, 1H n.m.r. (CDCl₃) 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 imes 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 ringopening. 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-nitroor 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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