# 2-Arylsulphonyl-3-phenyloxaziridines: a New Class of Stable Oxaziridine Derivatives

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*Summary* 2-Arylsulphonyl-3-phenyloxaziridines (**1a—d**), a new class of stable oxaziridine derivatives, are prepared by oxidation of the corresponding *N*-benzylidenearenesulphenamides (**2**) or sulphonamides (**3**) with *m*-chloroperbenzoic acid.

THERE is considerable interest in the chemistry of oxaziridines because of the unique properties this ring system demonstrates.[1,2] The ready thermal rearrangement of these compounds to amides and nitrones has hindered a study of their chemistry. Stable oxaziridines are limited to those compounds with the nitrogen substituted directly by carbon (*N*-alkyl, aryl, acyl compounds)[1-3] with an *N*-aryl group accelerating the rate of rearrangement to such an extent that most *N*-aryl oxaziridines are not isolable.[1-4] It is generally believed that the electron-attracting ability of the aryl group is responsible for this increase in reactivity.

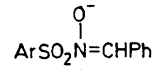
In this context, we report the synthesis and preliminary results of the thermal decomposition of a new class of stable oxaziridines, 2-arylsulphonyl-3-phenyloxaziridines (**1a—d**); the first stable example of this ring system containing an atom other than carbon attached to nitrogen.

(1)

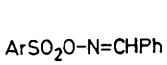


(2) $n = 0$
(3) $n = 2$

a; Ar = *p*-tolyl
b; Ar = Ph
c; Ar = 4-$ClC_6H_4$
d; Ar = 4-$NO_2C_6H_4$



(4)



(5)

The title compounds were prepared by oxidation of the corresponding *N*-benzylidenesulphenamide (**2**)[5] or sulphonamide (**3**)[6] with 5 and 2 equiv. respectively, of *m*-chloroperbenzoic acid. The oxaziridines (**1a—d**) are crystalline solids which gave satisfactory elemental analysis.† Their n.m.r. spectra are characterized by a singlet at $\delta$ 5·4—5·6 for the $\alpha$ proton, which remains a sharp singlet down to −70 °C. This indicates either a rapid equilibrium between the two isomeric forms or more likely a single isomer. Further evidence for the structures of (**1a—d**) is their reaction with triphenylphosphine to yield triphenylphosphine oxide and (**3**) in good yield. Reaction of (**1a—d**) with potassium iodide in acetic acid gave iodine in 96—100% yield.§

(1) $\xrightarrow{\text{heat}}$ { $ArSO_3H + ArSO_2NH_2 + ArSO_2OEt$ ; $+ PhCHO + PhCN$ ; $+ 4\text{-}NO_2C_6H_4SO_3H \cdot H\text{-}O\text{-}N{=}CHPh$ [from (1d)] }

(6)

SCHEME

Refluxing (**1a—d**) in non-purified chloroform (which contains small amounts of ethanol and water) for 5—48 h resulted in complex mixtures consisting of varying amounts of benzaldehyde (23—56%), benzonitrile (14—32%), and the corresponding sulphonic acid (45—75%), sulphonamide (5—25%), and ethyl sulphonate ester (12—30%), (Scheme). The oxaziridine (**1d**) gave an additional product (**6**) (m.p. 158—9 °C, 10—18%) identified as the 4-nitrobenzenesulphonic acid salt of benzaldehyde oxime.‡ Decomposition of (**1a**) in the presence of 4-nitrobenzenesulphonic acid gave (**6**) in 20% yield suggesting that the oxime is also an intermediate in the decomposition of (**1a—d**). The product composition appears to be sensitive to both solvent and reactant purity. In purified chloroform (free of ethanol and water) (**6**) and the ethyl sulphonate esters were not obtained.

The expected products of the thermal decomposition of (**1a—d**), *N*-benzoylarenesulphonamides,[7] which were shown to be stable under our reaction conditions, were detected only in trace amounts (t.l.c.). A mechanism for the rearrangement of oxaziridines to amides involving N–O bond cleavage and an intermediate nitrenium ion as proposed by Splitter and Calvin[2a] should be energetically unfavourable in (**1a—d**), while a developing negative charge on nitrogen as advocated by Lamchen[4] should be favoured. The traces of amides detected in the thermal decomposition of (**1a—d**) appear to be consistent with the former mechanism.

Several of the reaction products obtained in the thermal decomposition of (**1a—d**) can be explained in terms of known chemistry of oxaziridines. Rearrangement of (**1a—d**) to an *N*-sulphonyl nitrone (**4**), which would be expected to be highly reactive, followed by attack of water and ethanol on (**4**) would yield sulphonic acid, ethyl sulphonate ester, and benzaldehyde oxime. Similar products and a similar mechanism have been proposed for the acid and thermal reaction of *N*-(diphenylmethylene)methylthiomethylamine *N*-oxide.[8]

Rearrangement of (**4**) to (**5**), followed by disproportionation to sulphonic acid and benzonitrile, may explain the formation of these products. Rearrangement of nitrones to oxime-*O*-ethers is known[4,9] and disproportionation of (**5**) has been reported.[10] Under our reaction conditions (**5a**)[10] gave quantitative yields of toluene-*p*-sulphonic acid and benzonitrile. The isolation of *O*-anilinoformylbenzaldoxime from the thermal decomposition of 2-aminoformyloxaziridine has been reported.[2e] Attempts to detect (**4**) and (**5**) have failed.

Fragmentation of (**1a—d**) to yield a nitrene and/or radical intermediates can explain the formation of benzaldehyde, sulphonamide, and tar. Photochemically, oxaziridines yield carbonyl compounds and nitrenes.[11] The generation of arylsulphonylnitrenes in the presence of benzene often yields arenesulphonanilides in addition to sulphonamide.[12] In the presence of nitro groups these intermediates yield nitrogen dioxide.[12] While the evolution of $NO_2$ was noted in the decomposition of (**1d**), arenesulphonanilides were not detected when (**1a**) and (**1d**) were decomposed in benzene.

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† M.p., decomposition (°C); (**1a**), 87, (**1b**), 97; (**1c**), 92; (**1d**), 96.

‡ Compound (**6**) was prepared independently in 90% yield by the reaction of benzaldehyde oxime with an equivalent amount of 4-nitrobenzene sulphonic acid.

§ Release of $I_2$ from KI determined by titration with standard $Na_2S_2O_3$.

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