An Efficient Thermal Route to Arenesulphenylnitrenes

Robert S. Atkinson,* Michael Lee, and John R. Malpass*
Department of Chemistry, The University, Leicester LE1 7RH, U.K.

Arenesulphenylnitrenes are generated efficiently from sulphenamides, (**1**), on heating at *ca.* 80—120 °C and are trapped by alkenes as the corresponding aziridines in quantitative yield; this approach is shown to be more efficient and more widely applicable than the oxidation of arenesulphenamides but both reactions appear to involve the same nitrene intermediate.

The chemistry of nitrenes attached directly to a heteroatom (*N*-nitrenes, *S*-nitrenes *etc.*) is of continuing interest. Preparative methods, however, are based for the most part on oxidation of the corresponding amino-compounds with lead tetra-acetate (LTA) in which strongly oxidising, acidic conditions cannot be avoided. As a consequence of our work with such nitrenes[1] and with bridged azabicycles,[2] we have investigated the thermal extrusion of bridging nitrogen from 1,4-dihydro-1,4-iminonaphthalenes as a potential method for the unambiguous production of discrete nitrenes under gentle, neutral conditions.[3] We report here the smooth generation of arenesulphenylnitrenes from the sulphenamides (**1**) and their intermolecular trapping by alkenes.

Sulphenamides (**1**) were prepared as stable, crystalline compounds by treatment of 1,4-dihydro-1,4-iminonaphthalene with the appropriate arenesulphenyl chloride and pyridine in diethyl ether.† The 2,4-dinitrobenzenesulphenamide (**1a**) decomposed within 1 h at 120 °C in chlorobenzene solvent and, in the presence of styrene (3 mol. equiv.), a quantitative yield (n.m.r.) of aziridine (**7a**) was obtained. Recrystallisation gave a sample which was identical with authentic material[4] (mixed m.p.). Similar results were obtained for (**1b**)—(**1d**) but nitrene formation occurred at progressively lower temperatures as the number of nitro groups in the aryl ring was reduced. Using 3 molar equivalents of styrene, the yield of aziridine dropped to 50% for the conversion of (**1d**) into (**7d**) but in an excess of styrene, the yield was 100% (n.m.r.). The successful production of all four aziridines (**7a**)—(**7d**) emphasises an advantage of this method over LTA oxidation of the primary arenesulphenamides (**3**) which gave the aziridine in only one case [(**3a**): 38% yield of (**7a**)].[4] The failure of alkenes such as styrene to trap the nitrenes from oxidation of the other, less electron-deficient, arenesulphenamides was ascribed to the competitive interception of the nitrene by the sulphenamide sulphur in (**3**) leading ultimately to the formation of diaryl disulphides;[4] the tertiary arenesulphenamides (**1**) are evidently less nucleophilic and this diversion does not present a significant problem.

Surprisingly, the aziridines (**10a**) and (**10d**) are produced in 30—40% yield on heating (**1a**) and (**1d**), respectively, in methyl acrylate. Aziridines are not observed when the arenesulphenyl nitrenes are generated oxidatively from (**3**) in the presence of (**5**),[4] presumably as a result of the greater nitrenophilicity of (**3**) compared with methyl acrylate. The solvent requirements of the oxidative route are often such as

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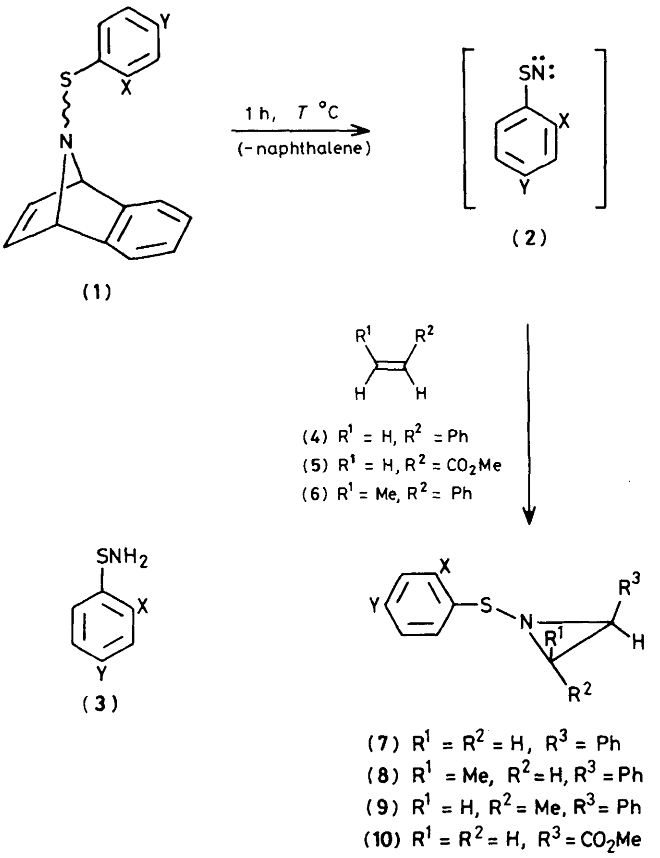
† Yields of (**1**) were highest for the more electron-deficient arenesulphenyl chlorides. In the case of (**1d**), further addition of benzenesulphenyl chloride to the 2,3-double bond also occurred. All new compounds showed spectroscopic properties which were in agreement with the proposed structures.



a; X = Y = NO_2
b; X = H, Y = NO_2
c; X = NO_2, Y = H
d; X = Y = H

Scheme 1. T (°C) 100—120 (**a**), 100 (**b**) and (**c**), 80 (**d**).

to limit the amount of alkene trap which is available in solution; the thermal extrusion route does not place any limit on the alkene concentration and yields of aziridine can therefore be raised dramatically.

Whilst it is not possible to generate nitrenes from (**1**) and (**3**) under similar conditions we have, nevertheless, strong circumstantial evidence for a common intermediate. Thus, oxidation of (**3a**) with LTA in the presence of (Z)-1-phenylpropene (**6**) gives the aziridines (**8**) and (**9**) in the characteristic ratio of *ca.* 3 : 1 under a variety of conditions.[4] Despite the temperature difference, the reaction of (**1a**) with (**6**) also led to (**8**) and (**9**) in a ratio which varied from *ca.* 3.0 : 1 to 2.6 : 1 depending on solvent, temperature, and alkene concentration. Furthermore, the unexpected proclivity of the nitrene (**2a**) derived from (**3a**) to react preferentially with the less-substituted double bond of 2-methylbutadiene[5] is also evident when (**2a**) is generated thermally.

The application of this extrusion route to the generation of other nitrenes which are inaccessible by traditional methods is being pursued. Considerable 'fine tuning' of the activation energy for cheletropic elimination of the nitrene should be possible by modification of the substituents present in the incipient naphthalene ring and by the use of other bridged polycyclic benzenoid hydrocarbons such as 9,10-dihydro-9,10-iminoanthracenes.

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