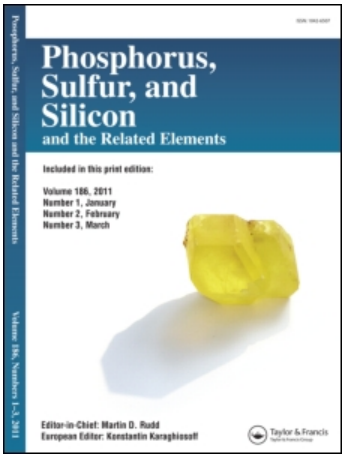

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Zwanenburg, B. , Philipse, H. J. F. , Verstappen, M. M. H. and Gieling, R. G.(1997) 'Sulfur substituted Small-ring Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 453 — 454
To link to this Article: DOI: 10.1080/10426509708545594
URL: http://dx.doi.org/10.1080/10426509708545594

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 453–454
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Sulfur substituted Small-ring Heterocycles

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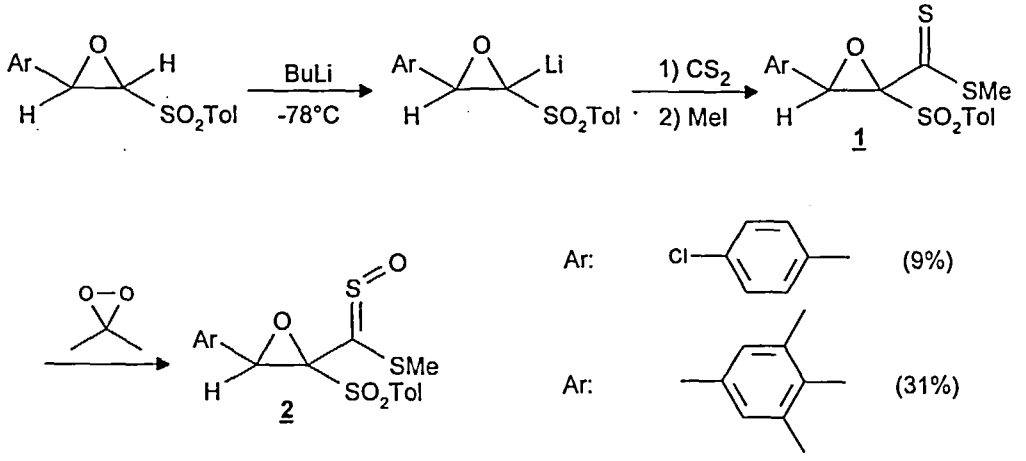
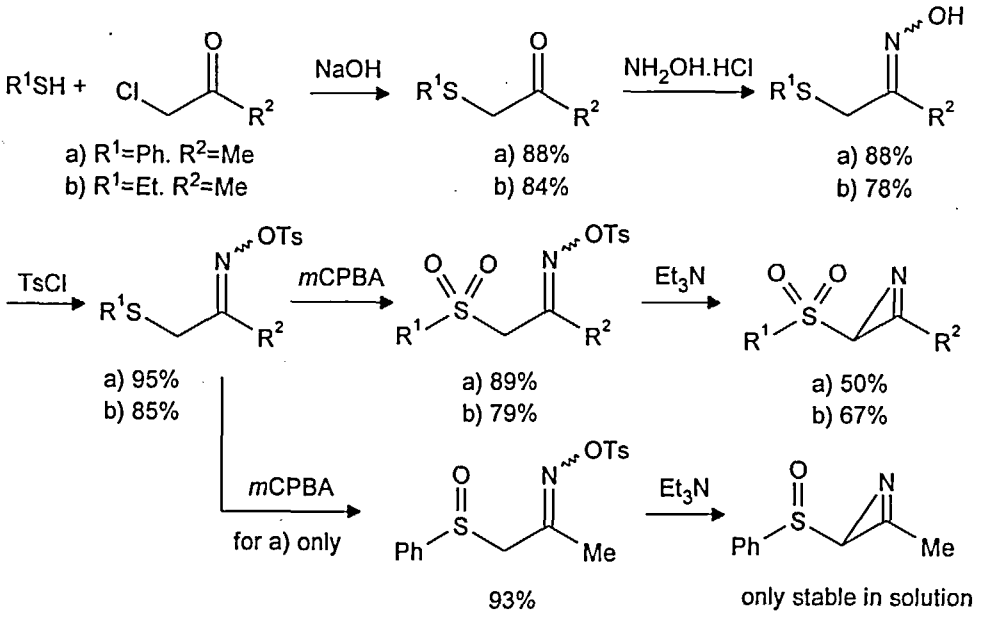
The synthesis of epoxy sulfines and sulfonyl azirines is described

Epoxy sulfines are of interest in connection with previous studies on epoxy ketenes[1] and epoxy isocyanates.[2] The synthesis of these sulfines was achieved starting from epoxy sulfones as shown in Scheme 1. The oxidation of the dithioester **1** to the sulfine **2** had to be carried out under mild conditions, namely with dimethyldioxirane as the oxidant. The geometry of the sulfine unit was established as indicated by an X-ray diffraction analysis. It was found that kinetic stabilization by bulky substituents is a prerequisite for the isolation of these epoxy sulfines. An intramolecular ring expansion which is a typical behavior of epoxy ketenes[1] and epoxy isocyanates[2] was not observed for epoxy sulfines.



Scheme 1

Sulfonyl azirines form a second class of sulfur substituted small-ring heterocycles that caught our interest. These compounds were synthesized starting from β-keto sulfides via a modified Neber reaction[3] involving a 1,3-elimination reaction of oxime tosylates. In the case of sulfonyl substituted oxime tosylates treatment with triethylamine smoothly gave sulfonyl azirines in the yields indicated in Scheme 2. The analogous conversion of sulfinyl substituted oxime tosylates proved to be more cumbersome, due to the inherent instability of the product. Sulfinyl azirines are only stable in solution. A spectral analysis of these products showed that no diastereomeric induction had taken place during the 1,3-elimination.



Scheme 2

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