

## SYNTHESIS OF ALLYLIC SULPHIDES AND SELENIDES BY LEWIS ACID MEDIATED DISPLACEMENT REACTIONS OF SULPHONES

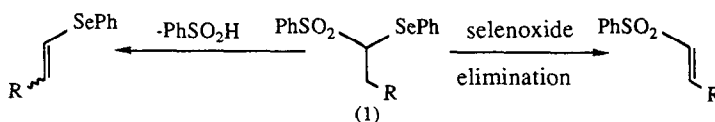
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ABSTRACT: Allylic sulphides or selenides are produced by reaction of appropriate  $\alpha$ -sulphonyl sulphides or selenides with allyltrimethylsilane in the presence of  $\text{EtAlCl}_2$ .

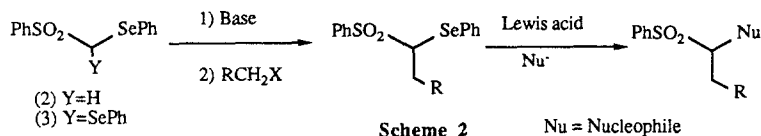
Sulphones have secured a central role in organic synthesis, due primarily to the versatility of their derived carbanions, for example in the Julia reaction.<sup>1</sup> The sulphone group has also become important in the activation of carbon-carbon double bonds; thus vinyl sulphones undergo smooth conjugate addition reactions with appropriate nucleophiles and take part in cycloaddition reactions.<sup>2</sup> In synthesis the sulphone group is often disposed of in a non-productive reductive step once its function has been served. Only rarely have sulphones been usefully employed as leaving groups in reactions forming new carbon-carbon bonds.<sup>3</sup> We describe here some new chemistry which utilises both the usual role of the sulphone as carbanion stabiliser, and illustrates its utility as a leaving group under Lewis acid catalysis.

We first became interested in  $\alpha$ -sulphonyl selenides of general structure (1) since they are potentially flexible precursors to both vinyl sulphones and vinyl selenides, Scheme 1.



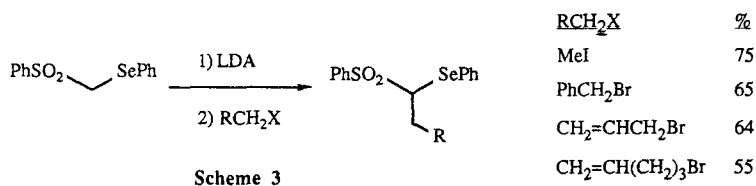
Scheme 1

Whilst this work was in progress a detailed study of vinyl sulphone synthesis appeared, including their preparation by direct selenation of sulphone carbanions to give compounds of type (1), followed by selenoxide elimination.<sup>4</sup> We decided to focus on a different type of chemistry of sulphonyl selenides (1) which would allow nucleophilic displacement of the sulphone, Scheme 2.



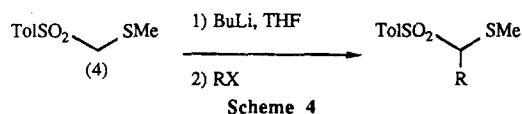
Trost showed quite recently that allylic sulphones could function as electrophiles in reactions with suitable Lewis acidic organometallics.<sup>5</sup> We hoped that the presence of a carbocation stabilising heteroatom  $\alpha$  to the sulphone would allow compounds such as (1) to react similarly.<sup>6</sup>

For the preparation of selenides (1) we preferred alkylation of the parent compound (2) rather than the selenation of sulphone carbanions. In our hands this latter process was inefficient, resulting in recovery of the starting sulphones, as well as products having more than one SePh group. Treatment of (2) with LDA in THF at  $-78^\circ\text{C}$ , followed by addition of a reactive alkylating agent (MeI, PhCH<sub>2</sub>Br, etc.) and warming to  $0^\circ\text{C}$  gave good yields of products (1), Scheme 3.

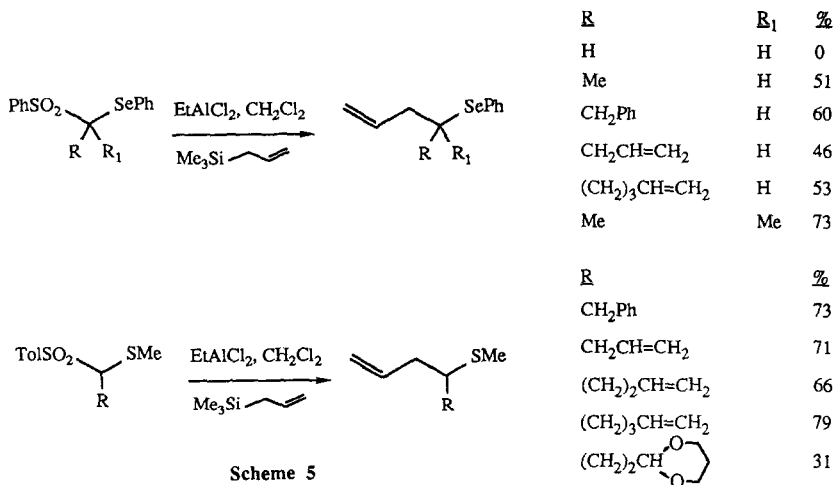


The use of less reactive alkylating agents necessitated the use of HMPA, and the yields were somewhat lower due to the formation of the diselenide (3) (m.p.  $97-99^\circ\text{C}$ ) as by-product, along with some deselenated materials.

We also synthesised some thiosulphones as substrates for our study. These were prepared by the straightforward and high-yielding alkylation of the commercially available sulphide (4), Scheme 4.<sup>7</sup>

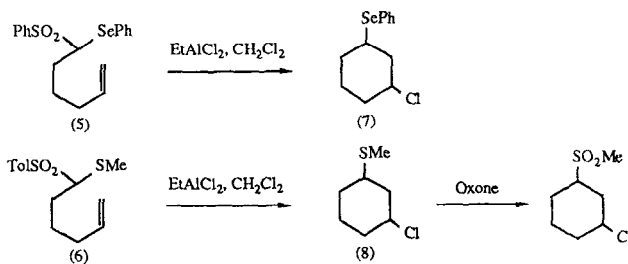


We initially examined the reactions of the sulphonyl selenides (1) with allyltrimethylsilane mediated by various Lewis acids. Of those tried, TiCl<sub>4</sub> and SnCl<sub>4</sub> were found too harsh,<sup>8</sup> whilst Et<sub>2</sub>AlCl and ZnCl<sub>2</sub> gave very sluggish reactions. Pleasingly, EtAlCl<sub>2</sub> was found to give very clean conversion of sulphones (1) into the desired allylated products, the results obtained using this method with both sulphonyl selenides and sulphides are shown in Scheme 5.<sup>9</sup>



Scheme 5

In each case the desired allylic sulphide or selenide was obtained in moderate to good yield, apart from the pentenyl substituted examples (5) and (6). In these cases the major non-polar product from the reaction was found not to have incorporated an allyl group, but to have cyclised to form the chlorocyclohexanes (7) and (8), respectively (e.g. for (8)  $m/z$  164 ( $M^+$ ), 129 ( $M^+-Cl$ ), 116 ( $M^+-MeSH$ )), Scheme 6.



Scheme 6

These cyclic products were again formed in good yield, but were rather difficult to separate from minor amounts of impurities. The sulphides were also obtained as a mixture of stereoisomers which made nmr assignment less than straightforward. We therefore took the mixture of isomeric sulphides, purified by distillation, and reacted it with Oxone<sup>®</sup> in MeOH/water to give the corresponding sulphones which were then easily separated using chromatography.<sup>10</sup>

This new method thus allows facile preparation of a variety of acyclic and cyclic sulphides and selenides, further developments to this chemistry are presently being explored.

#### Acknowledgements

We would like to thank Pfizer Central Research, Sandwich, Kent for financial support, and assistance in this project.

### References

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- 3) Julia has developed methods for replacement of vinylic sulphonyl groups with alkyl groups, see J. L. Fabre, M. Julia and J. N. Verpeaux, Bull. Soc. Chim. Fr., 1985, 772; cyclopropane formation using sulphone as leaving group is well established, e.g. G. Pattenden and D. A. Whiting, J. Chem. Soc., Perkin Trans. 1, 1975, 897; for other transition metal catalysed work see ref. 5 and references therein.
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- 7) K. Ogura, K. Otsuki, M. Nakamura, N. Yahata, K. Takahashi and H. Iida, Tetrahedron Lett., 1985, **26**, 2455.
- 8) Use of these Lewis acids resulted in formation of allylphenylselenide as a difficult-to-separate by-product.
- 9) In a typical procedure the starting sulphone (1 mmol) and allyltrimethylsilane (5 mmol) were dissolved in dry dichloromethane (3 ml) and the mixture cooled to  $-78^{\circ}\text{C}$  before addition of  $\text{EtAlCl}_2$  (2 ml of 1M solution in hexane). The mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h and then warmed to  $0^{\circ}\text{C}$  and the reaction monitored by TLC. When all starting sulphone was consumed (1-5 h depending on substrate) the mixture was poured into 2M HCl and extracted into ether. The ether layer was washed successively with 2M HCl, 2M NaOH, and brine. After drying ( $\text{MgSO}_4$ ) and evaporation of the solvent the product was isolated by flash column chromatography.
- 10) Analysis of the high field NMR spectra of these compounds indicated that the major product was the *cis* isomer, the yield of the two products being 59% and 20% respectively.

(Received in UK 26 October 1988)