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Episulfone α-Anions: Preparation and Synthetic Applications

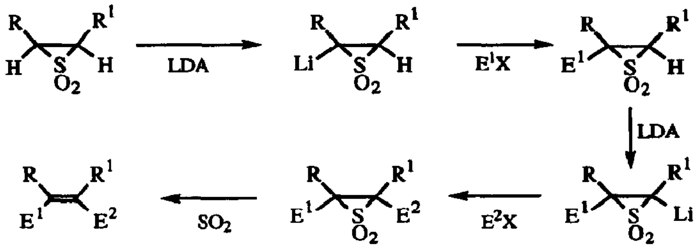
Andrew E. Graham,[a] Wendy A. Loughlin,[b] and Richard J. K. Taylor[a*]

[a]Department of Chemistry, University of York, York YO1 5DD, UK
[b]School of Chemical Sciences, University of East Anglia, Norwich
NR4 7TJ, UK.

Abstract: Monosilyl-, monostannyl-, disilyl- and distannyl-episulfones have been prepared by episulfone α–anion generation followed by trapping with the appropriate electrophilic reagent. Elimination of sulfur dioxide provides a new route for the preparation of vinyl silanes and vinyl stannanes.

We have recently reported[1] a modification of the Ramberg-Bäcklund reaction[2,3] which enables a range of functionalised episulfones to be prepared from α–halo-sulfones in high yield.[4] Given the ready availability of these compounds and their surprising stability,[1] we decided to investigate their potential as synthetic intermediates. In view of the synthetic importance of α–sulfonyl anion chemistry,[3] we commenced our studies in this area.[5,6] In principal, such methodology should provide a potentially useful new procedure for alkene synthesis, as illustrated in Scheme 1 with 1,2-dialkylated episulfones as starting materials.

Scheme 1



In this *Letter* we report the successful implementation of this sequence using silicon and tin electrophiles. This sequence leads ultimately to vinylsilanes, vinylstannanes and 1,2-disilylalkenes *via* the intermediacy of the corresponding isolable, silylated and stannylated episulfones (Scheme 2).[7] Episulfone (**1**) was chosen to test the methodology due to its accessibility[1] and the fact that alkene stereoisomers are not possible, thus simplifying the analysis of product mixtures. A number of base-solvent combinations were investigated for episulfone anion generation, but subsequent trapping with a range of electrophiles gave mainly episulfone decomposition and only a limited amount of anion trapping.[6a,8] We next investigated *in situ* trapping using trimethylsilyl chloride. Synthetically useful yields were obtained when LDA was employed as the base with varying amounts of monosilyl- and disilyl-episulfones (**2a**) and (**3a**) being obtained depending on the reaction stoichiometry (Table).

Table : Yields of (**2**) and (**3**)[a,b]
a. E = SiMe$_3$; b. E = SiEt$_3$; c. E= SnMe$_3$; d. E = SnBu$_3$

Reagents	Products	
2.2 LDA, 2 Me$_3$SiCl	(**2a**), 46-54%	(**3a**), $\leq$ 6%
2.2 LDA, 5 Me$_3$SiCl	(**2a**), c	(**3a**), 70%
1.5 LDA, 2 Et$_3$SiCl	(**2b**), 67%	(**3b**), c
2.2 LDA, 5 Et$_3$SiCl	(**2b**), 69%	(**3b**), c
2.2 LDA, 2 Me$_3$SnCl	(**2c**), 35%	(**3c**), 15%
2.2 LDA, 5 Bu$_3$SnCl	(**2d**), 52%	(**3d**), -

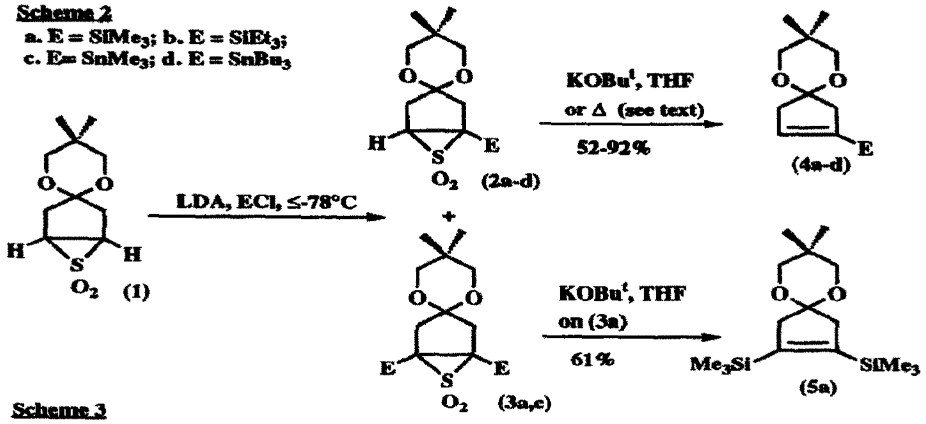
[a] For a representative experimental procedure see note 9.
[b] Contamination by tin by-products was observed in (**2c,d**) & (**3c**)
[c] Trace amounts were present in the crude products according to mass spectrometry.

The optimum conditions involved slow addition of the base (motor-driven syringe pump) to a stirred mixture of the episulfone and trimethylsilyl chloride in THF at $\leq$-78°C. Remarkably, given the degree of steric compression involved, with excess base and and a large excess of electrophile, the 2,3-bis(trimethylsilyl)-episulfone (**3a**) was formed in good yield (70%). Other electrophiles were also investigated (Table). With Et$_3$SiCl and Bu$_3$SnCl only monoaddition was observed to give (**2b**) and (**2d**), respectively, even when excess trapping agent was employed. This presumably reflects the increased steric hindrance in these examples. With Me$_3$SnCl a mixture of (**2c**) and (**3c**) was obtained. Steric hindrance around the episulfone seems to be the key factor in determining whether 1,2-disubstitution is observed as episulfone anion generation-Et$_3$SiCl trapping starting from trimethylsilylepisulfone (**2a**) proceeded to give the mixed disilylepisulfone (**6**) in high yield whereas the complementary reaction, commencing from the triethylsilyl-episulfone (**2b**) gave no trace of (**6**) (Scheme 3). Given that the corresponding 2-alkyl-episulfones could not be isolated,[1] the 2-silyl/stannyl and 2,3-disilyl/stannyl-episulfones proved to be surprisingly stable: they were purified by column chromatography and could be stored at -20°C for extended periods. These episulfones did slowly decompose to give the corresponding alkenes and this process could be carried out efficiently in boiling THF. The silylated episulfones were also converted to the corresponding alkenes using KOBu^t/THF but these conditions gave extensive decomposition with the stannylated episulfones.

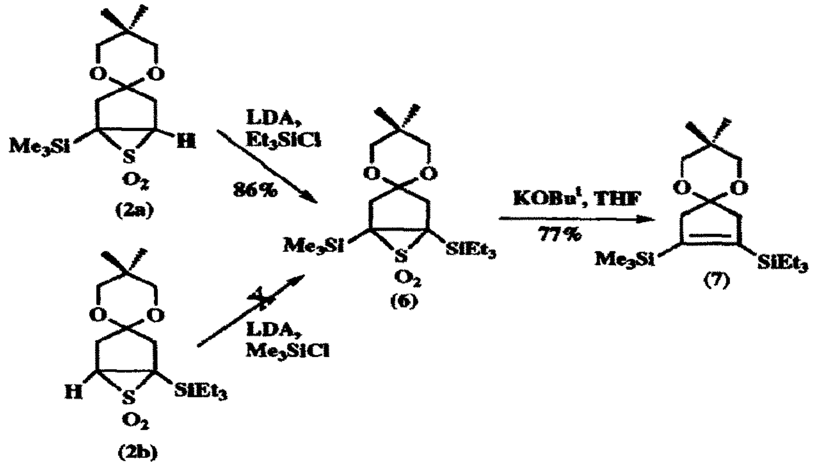
Disilylepisulfone (**3a**) underwent smooth desilylation on treatment with Bu$_4$NF giving episulfone (**1**) and further demonstrating the robustness of these compounds (Scheme 4). With CsF[10] desilylation was more controlled and some of the monosilylated compound (**2a**) was isolated. Application of these conditions to the mixed disilylepisulfone (**6**) gave selective removal of the trimethylsilyl group as shown. These observations augur well for trapping with electrophiles other than protons.[10] This area is under current investigation, as are

Scheme 2

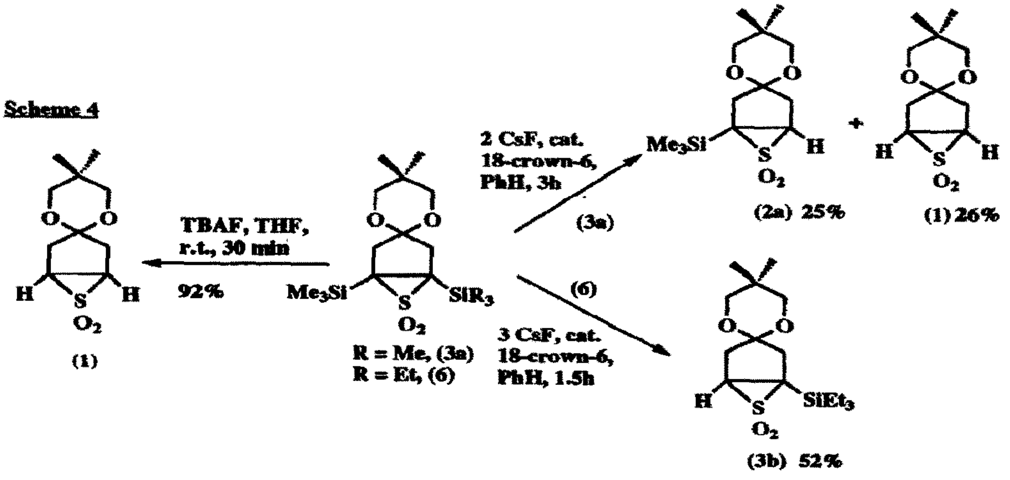
a. E = $SiMe_3$; b. E = $SiEt_3$;
c. E= $SnMe_3$; d. E = $SnBu_3$



Scheme 3



Scheme 4



studies to determine the synthetic utility of the vinylsilanes/stannanes (**4a-d**), (**5a**) and (**7**). In addition, the use of functionalised acyclic episulfones[1] in similar transformations is being investigated with a view to establishing the stereochemical preferences of the episulfone anion trapping reactions.

Acknowledgements

We are grateful to the S.E.R.C. and the University of York for the award of postdoctoral grants to Drs. Loughlin and Graham, respectively. We also thank Dr. S. M. Pyke for carrying out the initial experiments in this area, which will be reported in a full paper, and Dr. N. S. Simpkins (University of Nottingham) for sending us a preprint of his related work.

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5. Base-catalysed deuterium exchange reactions of episulfones have been reported (Bordwell, F. G.; Williams, J. M.; Hoyt, E. B.; Jarvis, B. B. *J. Am. Chem. Soc.*, 1968, **90**, 429.
6. (a) Preliminary results in this area were reported in 1991 (Jeffery, S. M.; Pyke, S. M.; Sutherland, A. G.; Taylor, R. J. K. Poster presentation at the The First Anglo-Norman Chemistry Colloquium, Rouen, 1991);
   (b) Dr. N. S. Simpkins (University of Nottingham) has informed us of his related studies in this area.
7. All new compounds gave consistent spectral and analytical/mass spectrometric data.
8. Other bases tried included BuLi, t-BuLi, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, NaH and KH; Other silylating agents (*e.g.* Me_3SiI, t-$BuMe_2SiCl$, t-$BuMe_2SiOTf$, Et_3SiOTf) failed to give the required products or gave only low yields.
9. Representative procedure: Episulfone (1, 200 mg, 0.86 mmol) was dissolved in THF (10 ml) and trimethylsilyl chloride (0.5 ml, 3.94 mmol) was added and the reaction cooled to -78°C. To this was then added LDA (2.2 equiv) in THF (10 ml) dropwise over a period of 30 min *via* a motor-driven syringe pump. Once addition was complete, the reaction was quenched at -78°C with 10% NH_4OH/NH_4Cl and then allowed to warm to room temperature. A standard work-up (CH_2Cl_2) gave the crude product as a yellow oil. Column chromatography (2 --> 5% ethyl acetate-petrol) gave 8,8-dimethyl-6,10-dioxa-2,3-bis(trimethylsilyl)-2,3-epithiaspiro[4.5]decane S,S-dioxide (**3a**) (223 mg, 70%) as a white solid, m.p. 75 - 76°C; Found: C, 51.2; H, 8.4; S, 8.7. $C_{16}H_{32}O_4Si_2S$ requires C, 51.02; H, 8.56; S, 8.51%; R_f 0.35 (ethyl acetate-petrol, 1:9); v_{max}(soln. in $CHCl_3$)1396 and 1364, 1327, 1153, 1116 cm^{-1};^1H NMR ($CDCl_3$, 270 MHz) 0.27 (18H, s, $SiMe_3$), 0.93 (6H, s, 8-Me_2) 2.45-2.65 (4H, m, 1-CH_2 and 4-CH_2), 3.88 (2H, s, 7-CH_2), 3.91 (2H, s, 9-CH_2); ^{13}C NMR ($CDCl_3$, 67.5 MHz), 0.28 ($SiMe_3$), 22.30 (C_8-Me_2), 29.94 (C-8), 38.44 (C-1, C-4), 52.98 (C-2, C-3), 71.23 and 73.55 (C-7 and C-9), 113.37 (C-5); *m/z* (CI) 313 [100%, $(M-SO_2)^+$].
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