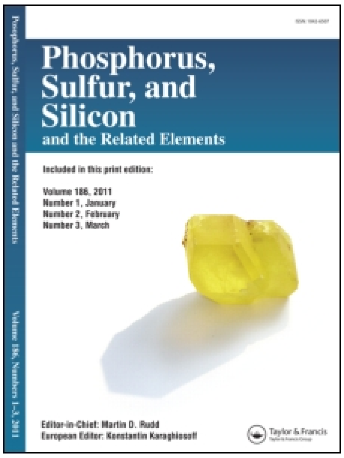

Phosphorus, Sulfur, and Silicon and the Related Elements

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 Schwan, Adrian L. and Refvik, Mitchell D.(1994) 'Preparation and Reactions of Substituted Ethenesulfenate Anions', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 327 — 328

To link to this Article: DOI: 10.1080/10426509408034222

URL: http://dx.doi.org/10.1080/10426509408034222

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 327–328
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PREPARATION AND REACTIONS OF SUBSTITUTED ETHENESULFENATE ANIONS

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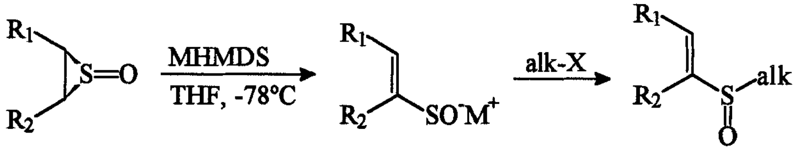
Abstract ***Trans*-alkyl and *gem*-silyl substituted ethenesulfenate anions result from the reaction of hexamethyldisilazide bases with *anti*-alkyl and *anti*-silyl substituted thiirane-S-oxides, respectively, via a stereoselective deprotonation process. The sulfenates can be captured at sulfur with certain alkyl halides or they can be converted to a series of substituted ethenesulfenic acid amides.**

INTRODUCTION

With a few exceptions, the chemistry of ethenesulfenate anions remains relatively unexplored, probably because of the lack of a general means of generating them. Some of our previous work[1] and that of Bonini *et al.*[2] suggested the reaction of amide anions with thiirane-S-oxides may provide a suitable route to the ethenesulfenate anions.

RESULTS

It was determined that the reaction of lithium or sodium hexamethyldisilazide (HMDS) with *anti*-alkyl thiirane-S-oxides is an excellent means of generating E-alkenesulfenate anions. They were readily captured at sulfur to afford E-alkenyl sulfoxides. Several

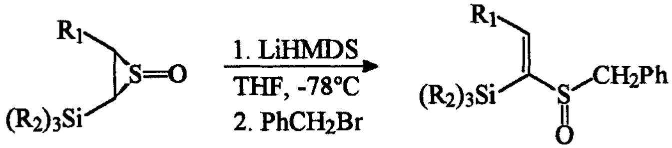


R_1 = H, Me, $nC_{11}H_{23}$, nBu, cC_6H_{11}, $TIPSCH_2$, But-3-enyl; R_2 = H: 60-80%
$R_1 = R_2$ = Et: 66%;, $R_1, R_2 = -(CH_2)_4-$: 75%

SCHEME 1 Synthesis and capture of alkyl substituted ethenesulfenate anions.

alkyl substituted ethenesulfenates could be produced, as shown in Scheme 1.[3] Deuterium labelling has revealed that the ring opening of the thiirane-S-oxides proceeds without inversion of the carbanionic centre and hence is a stereoselective process.

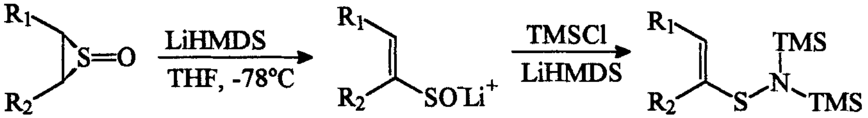
Anti-silyl thiirane-S-oxides can also be ring-opened cleanly under similar conditions. However the product is exclusively the geminally substituted silyl ethenesulfenate (Scheme 2).



R_1 = H; R_2 = Me, Et, Ph: 35-58%
R_1 = nBu; R_2 = Me: 57%; R_1 = nBu; $(R_2)_3Si$ = TBDMS: 54%

SCHEME 2 Synthesis and capture of silyl substituted ethenesulfenate anions.

The reaction of the *trans*-alkyl ethenesulfenates with TMSCl resulted in clean formation of E-alkyl-N,N-bis(trimethylsilyl) ethenesulfenamides in 26-59% isolated yield. The sulfenamides are believed to arise from initial formation of a trimethylsilyl ethenesulfenate ester which reacts with the hexamethyldisilzane already present in solution. Indeed, idealized conditions involve addition of extra LiHMDS before or after addition of the TMSCl (Scheme 3). The silylated sulfenamides can be desilylated and functionalized to yield ethenesulfenimines and acylated ethenesulfenamides.



R_1 = H, Me, $nC_{11}H_{23}$, nBu, cC_6H_{11}, But-3-enyl, $Ph(CH_2)_2$; R_2 = H: 26-59%
R_1 = R_2 = Ph: 54%; R_1, R_2 = $-(CH_2)_4-$: 49%

SCHEME 3 Synthesis of alkyl substituted ethenesulfenamides.

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