Tetrahedron Letters, Vol. 34, No. 18, pp. 2867-2870, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

STEREOSELECTIVE PREPARATION OF VINYL SULFONES BY PROTODESILYLATION OF ALLYL SILANES

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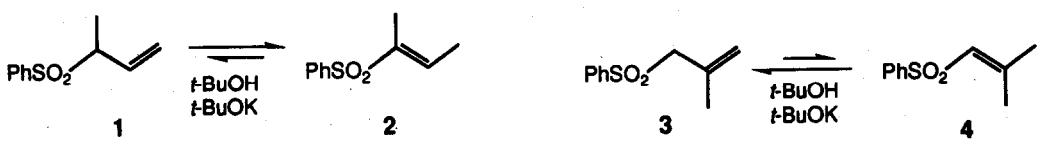
Abstract: Allyl sulfones can be conjugated to furnish vinyl sulfones via allyl silane intermediates. The stereoselectivity observed in the protodesilylation step provides a new method for stereoselective preparation of (E)-di- and trisubstituted vinyl sulfones.

Vinyl sulfones have enjoyed extensive application in organic synthesis due to the reactivity imparted to the alkene by the phenylsulfonyl group.[2] Vinyl sulfones are excellent substrates for Michael additions,[3a] cycloaddition reactions,[4] and elimination reactions.[5] In addition, methods have also been developed for the reductive removal of the sulfone moiety[6] which constitute new strategies for stereospecific alkene synthesis.

The aforementioned methodology relies upon efficient and stereoselective construction of the precursor vinyl sulfones, and numerous strategies have been developed in this regard.[2] In principle , one particularly attractive approach to vinyl sulfones would involve simple conjugation of the readily available (*vida infra*) allyl sulfones. However, this isomerization is favored in only a few systems [7a-c] since the β,γ-unsaturated sulfones are usually thermodynamically more stable than the coresponding α,β unsaturated isomers.[7] For example,

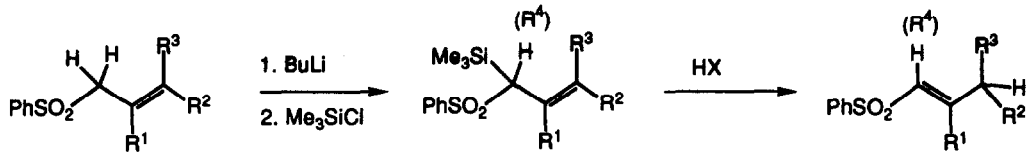


1 2 3 4

while Meyers has shown that the base-catalyzed equilibration (*t*-BuOK, *t*-BuOH, 25°C) of allyl sulfone **1** affords only the vinyl sulfone **2**, equilibration of the structurally isomeric allyl sulfone **3** provides a more typical 70:30 mixture favoring the allyl sulfone **3**[7a]. However, a kinetically controlled isomerization would thwart this unfavorable thermodynamic preference. We report herein a stereoselective two-step protocol which constitutes a solution to this problem.

The general strategy for conversion of allyl sulfones **5** to vinyl sulfones **7** is outlined in Scheme I and the various examples that have been examined are collected in Table I. The anions derived from allyl sulfones **5** undergo smooth silylation exclusively on the carbon adjacent to the phenylsulfonyl group. The resulting allyl silanes **6** are then subjected to carefully controlled protodesilylation reactions using either triflic acid

Scheme I

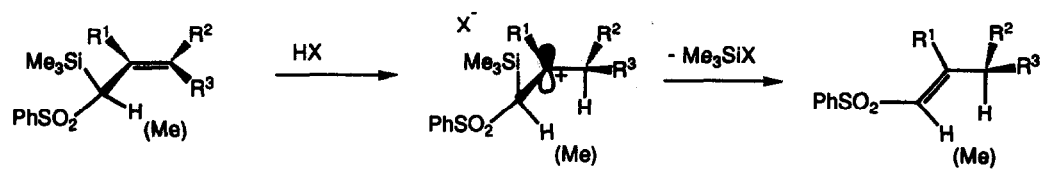


5 **6** **7**

or p-toluenesulfonic acid (1 equiv) in toluene or benzene, respectively, to afford the desired vinyl sulfone **7**. The reaction is quenched (sat. $NaHCO_3$) immediately upon disappearance of the allyl silane **6** (TLC). Extended reaction periods and/or the use of CH_2Cl_2 as solvent for these reactions gave, in some instances, deconjugated products and inferior *E/Z* ratios which presumably arose by subsequent acid catalyzed equilibration processes.

The protodesilylation reactions also proceed with high stereoselectivity as well as regioselectivity. In all cases where stereoisomers are possible (entries *a,c,d,e,h*) the *E* stereoisomer is the major, if not exclusive, product.[9] The stereochemical outcome of these protodesilylation reactions is consistent with the explanation provided for other electrophilic substitution reactions of allyl silanes[8] (Scheme II). Thus, the electrophile

Scheme II



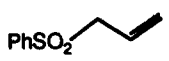
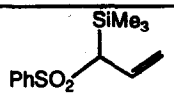
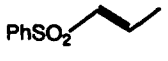
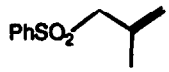
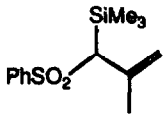
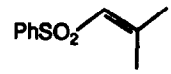
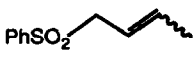
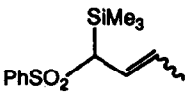
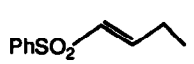
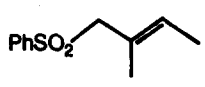
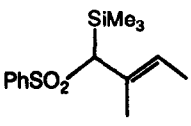
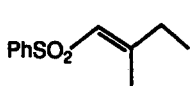
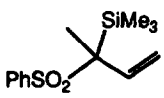
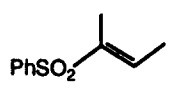
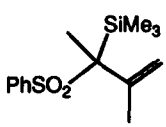
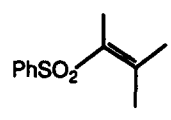
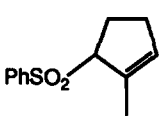
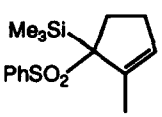
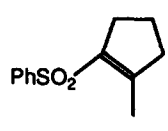
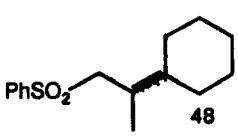
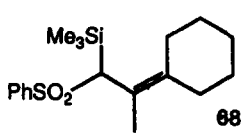
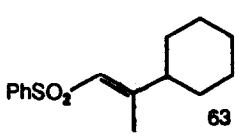
A **B** **C**

(proton) usually approaches the alkene from the face opposite the large electropositive silyl group in the preferred conformer A wherein the smallest allylic substituent (hydrogen or methyl) is eclipsing the double bond. "Least motion" bond rotation leads to intermediate cation **B** which is hyperconjugatively stabilized and thus provides a low energy pathway for loss of the silyl group, resulting in the *E* geometry as depicted in **C**.

In conclusion, it is now well appreciated that a trimethylsilyl moiety can serve in the capacity of a surrogate proton. In this case, protodesilylation reactions of α-phenylsulfonyl allyl silanes facilitates the stereoselective conjugation of β,γ-unsaturated sulfones to afford the respective vinyl sulfones virtually free of isomeric contaminants.

Acknowledgement: We appreciate the financial support provided by The National Institutes of Health.

Table I. Conjugation of β,γ-Unsaturated Sulfones by Protodesilylation of Allyl Silanes

Entry	β,γ-Unsaturated Sulfone[a]	Yield %	Allyl Silane[b]	Yield %	Conditions[c] Acid, Temp. Time	Vinylsulfone	Yield %	Ratio E:Z
a.		82		96	TfOH, 27°C, 12h		92	93:7
b.		85		88	TsOH, 60°C, 12h		84	
c.		84		77	TfOH, 27°C, 12h		94	100:0
d.		78		85	TfOH, -30°C, 3h		95	90:10
e.				84[d]	TsOH, 70°C, 24h		92	100:0
f.				96[d]	TsOH, 55°C, 12h		98	
g.					TsOH, 70°C, 12h		40[e]	
h.		48		68	TfOH, -10°C, 1h		63	100:0

[a]Prepared from the corresponding allylic halide and sodium benzenesulfinate in DMF. [b]1.1 equiv nBuLi, 0°C, THF 10 min; 2 equiv chlorotrimethylsilane, -78°C. [c]Protodesilylation was performed using p-toluenesulfonic acid or triflic acid (1 equiv) in benzene or toluene, respectively. [d]Prepared by methylating the corresponding α-trimethylsilylsulfone (1.1 equiv BuLi, 0°C, THF, 30 min; 3 equiv CH_3I, -78°C to R.T.). [e]Yield for three steps (phenylsulfonylation of the corresponding bromide, silylation, and protodesilylation).

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1. Fellow of the Alfred P. Sloan Foundtion, 1985-1987; address correspondence to Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802.

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9. The stereochemical assignments of the vinyl sulfones are based on the diagnostic resonances in the ^1H NMR spectra, in particular, resonances at δ 2.13 and δ 1.87 for the methyl protoms syn and anti to the phenylsulfonyl group, respectively. All new compounds reported herein exhibit satisfactory spectral (IR, NMR), analytical and/or high resolution mass spectral characteristics.

(Received in USA 2 February 1993)