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CONVERSION OF VINYL SULFONES TO REGIOSPECIFICALLY FUNCTIONALIZED TRISUBSTITUTED OLEFINS.¹

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Abstract: Conjugate-addition of phenyldimethylsilyllilthium (or cuprate) to vinyl sulfones followed by in situ alkylation of the α -sulfonyl anion provides α -alkylated β -silyl sulfones. Treatment of these materials with fluoride provides trisubstituted olefins via the Kocienski olefin synthesis.

In connection with our vinyl sulfone program we wished to effect conversion of γ -alkoxyvinyl sulfones **1-3** to alkylated olefins **6** (X=OR). In theory, reductive cleavage of the sulfone moiety could produce a vinyl anion which might be alkylated to afford the target compounds. In practice, Yus has recently demonstrated that phenyl vinyl sulfones suffer preferential rupture of the sulfur-aryl bond upon reaction with lithium metal in the presence of naphthalene, thereby leading to phenyl-lithium rather than a vinyllithium reagent.² An equivalent two-pot transformation would seem to be possible via conjugate-addition of phenyldimethylsilyl anion^{3,4} followed by electrophilic trapping of the intermediate α -sulfonyl anion to afford β -silyl sulfone **4**. Completion of the process would then involve fluoride-mediated 1,2-elimination of fluorosilane and phenylsulfinate via the popular Kocienski olefin synthesis.⁵ As can be seen in scheme 1 and the table, those substrates bearing a γ -alkoxy group are susceptible to competitive β -elimination at the stage of putative intermediate siliconate anion **5**, surprisingly providing a mixture of allyl ether **6** and alkylated allyl sulfones **7**.

Scheme 1 SO ₂ Ph	1a) PhMe ₂ SiLi, THF Z E -78°C, 0.25h 1b) Electrophile, X $(CH_2)_n$	$X \xrightarrow{E} (CH_2)_n$ and/or	E SO ₂ Ph (CH ₂) _n
1 n=1 2 n=2 3 n≖3	2) $(n-Bu)_4NF$ $\begin{pmatrix} 4 & Z= & SiMe_2Ph \\ THF & reflux & 5 & Z= & SiMe_2Ph \\ 2 - 3 & h & PF \\ \end{pmatrix}$	6	7

SM	X=	1b) THF/HMPA, -78°C + Electrophile	% Yield 4	% Yield 6	% Yield 7
1	OTBDMS	CH ₂ =CHCH ₂ Br	4a 87%@,#,‡	6a 60%* X=H	
1	OTBDPS	TBDMSO(CH ₂)7CH=CHCH ₂ Br [#]	4b 69%@,#,‡	6b 98% [¢] X≕H	
2	OMe	PhCH ₂ Br	4c 98%	6c 96%	•
2	OMe	CH ₂ =CHCH ₂ Br	4d 98%	6d 37%*	7d 25%
2	омом	CH ₂ =CHCH ₂ Br	4e 73% [@]	6e trace*	7e 80%
2	омом	– PhCH2Br	4f 75%@	6f 70%	7f 27%
3	н	PhCH2Br	4g 95%	6g 97%	•••
3	OMe	PhCH ₂ Br	4h 74% [@]	6h 98%	

@Remainder of product is proton-quenched β-silyl sulfone adduct; [‡]1 only provides 72% deuterium incorporation (4,E=D) when treated with D₂O, while 2 provides 88% deuterium incorporation; [#]6:1 E/Z mixture; ^ΦIsolated as the bis alcohol with both silyl ethers having undergone concomitant desilylation; ^{*}Volatility losses.

This strategy can readily be applied for the net reductive cleavage of the sulfone moiety. For example, conjugate-addition of phenyldimethylsilyllithium to tetracyclic sulfones 8^6 and 9^7 followed by aqueous quenching provides β -silyl sulfones 10 and 11, respectively. Completion of the synthesis of olefins 12 and 13 smoothly follows upon fluoride treatment (Scheme 2).



A final example which demonstrates both the scope and limitations of this method is seen in scheme 3. Conjugate-addition of phenyldimethylsilyl cyanocuprate to bicyclic sulfone 14⁸ provides tricyclic sulfone 16 in a yield of 66%. Fluoride treatment once again gives a mixture of the Kocienski olefin product 17 and the unwanted allylic sulfone 18, presumably via competitive β -eliminations at the stage of the pentavalent siliconate intermediate.



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References and notes

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⁷Prepared in 78% overall yield from 8 by isomerization to the allylic sulfone, osmylation,

conversion to the carbonate with triphosgene, treatment with DBU, and silvlation.

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