

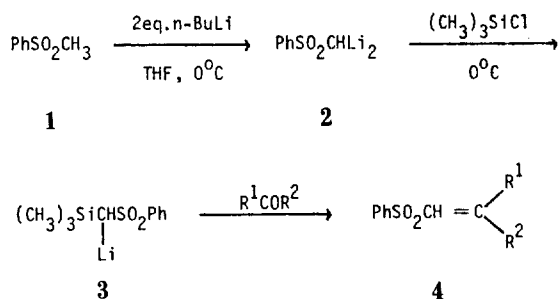
Facile Synthesis of Vinyl Sulfones From Methyl Phenyl Sulfone

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The importance of vinyl sulfones in organic synthesis is now well established.¹ Their diverse reactivities² include conjugate addition, cycloaddition and deprotonation reactions. A few synthetic methods were reported for these compounds.³ The elimination reactions of β -halosulfones which might be prepared from the addition of sulfonyl halides to alkenes were limited by the availability of the starting β -halosulfones and severe reaction conditions in the elimination step. The carbo-olefination methods using α -sulfonyl-methanephosphonates *via* Wittig-Horner reaction and α -(trimethylsilyl)methyl sulfones *via* Peterson reaction are good candidates for the synthesis of the vinyl sulfones, but have the disadvantage that the starting materials mentioned above are prepared in the multistep sequence. During our studies to minimize steps for the synthesis of vinyl sulfones using sulfone dianion, we have reported⁴ the synthesis of vinyl sulfones by in situ Wittig-Horner reaction *via* phosphorylation of the α, α -dilithiosulfone.⁵ In this case, however, ketones were failed to give vinyl sulfones at low temperature.



Here we now wish to report a facile synthesis of vinyl sulfones from methyl phenyl sulfone (1) at low temperature. Treatment of trimethylsilyl chloride to the dianion (2) which is generated by the addition of 2 eq. *n*-BuLi to methyl phenyl sulfone (1) leads to corresponding silylated anion (3). The resulting anion (3) reacted with various carbonyl compounds to give the desired vinyl sulfones. The results are summarized in Table. In the reaction of anion (3) with aromatic aldehydes vinyl sulfones were obtained in high yields and (E)-isomer was major product. Also the reaction of anion (3) with ketones gave trisubstituted vinyl sulfones. In the case of enolizable carbonyl compounds the trimethylsilyl anion (3) could also act as a base⁶ and α -(trimethylsilyl)methyl phenyl sulfone was obtained in a small amount.

A typical experimental procedure is as follows: A solution of methyl phenyl sulfone (1 mmol) in 6 ml of anhydrous THF was treated dropwise with a solution of 1.6 M *n*-butyllithium (2 mmol) in hexane at 0°C. After 30 min of stirring at 0°C, a solution of trimethylsilyl chloride (1 mmol) in 2 ml THF was added dropwise. The reaction mixture was stirred for 30 min at 0°C, then cooled at -78°C. To the resulting clear yellow

Table Preparation of Vinyl Sulfones (4) from Methyl Phenyl Sulfone (1)

No	R ¹	R ²	Condition	Yield (%) ^a	E/Z ^b
a	C ₆ H ₅	H	-78°C, 2h	80	93:7
b	<i>p</i> -CH ₃ O-C ₆ H ₄	H	-78°C, 2h	82	94:6
c	<i>p</i> -Cl-C ₆ H ₄	H	-78°C, 2h	85	95:5
d	2-Furyl	H	-78°C, 2h	83	92:8
e	CH ₃ (CH ₂) ₅	H	-78°C, 2h	70	50:50
f	CH ₃ (CH ₂) ₄ -	CH ₃	0°C, 3h	72	50:50
g	-(CH ₂) ₅ -		0°C, 3h	75	—
h	C ₆ H ₅	C ₆ H ₅	0°C, 3h	80	—

^a Isolated yield. ^b E/Z ratios were determined by GLC and ¹H-NMR.

solution, benzaldehyde (1 mmol) in 2 ml THF was added and stirred at -78°C for appropriate time. The reaction mixture was poured into 5 ml of saturated aqueous NH₄Cl and extracted with three 10 ml portions of ether. The combined extract was successively washed with 5 ml portions of H₂O, saturated NaHCO₃, and brine, dried over MgSO₄, and evaporated under reduced pressure. Vinyl sulfones were purified by column chromatography on silica gel and characterized by IR, ¹H-NMR and mass spectral data.⁷

In conclusion, the present method provides a short passage for the synthesis of various vinyl sulfones.

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- Representative characteristics of 4g ¹H-NMR (CDCl₃) δ 1.58(6H, br), 2.17(2H, br), 2.70(2H, br), 6.16(1H, br s), 7.40-7.70(3H, m), 7.80-8.00(2H, m), IR(film) 3060, 2925, 2857, 1620, 1585, 1310 and 1140 cm⁻¹, Mass. *m/z* 236(M⁺) and 77 (100%).