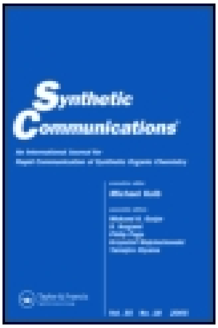

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ONE-POT SYNTHESIS OF α-METHYL VINYL SULFONES FROM ETHYL PHENYL SULFONES

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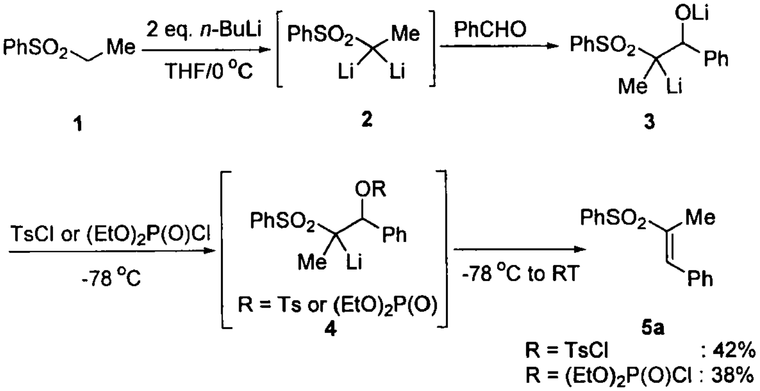
ABSTRACT: Various α-methyl vinyl sulfones were synthesized by Horner-Emmons olefination of aldehydes and sulfonyl phosphonate generated from 1,1-dilithiosulfone.

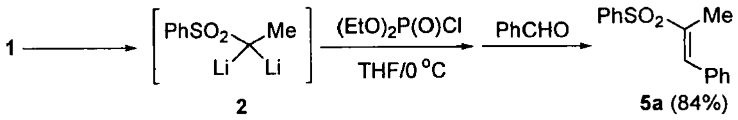
The importance of vinyl sulfone in organic synthesis has been well established.[2] Much effort has been made to develop the preparation of vinyl sulfones. Olefination of carbonyl compounds *via* Horner-Emmons reaction[3] or Peterson reaction[4] has been documented for the conversion of carbonyl compounds to vinyl sulfones. Selenosulfonation of olefins and the subsequent elimination gives vinyl sulfones.[5] The elimination reaction of β-halosulfones prepared from the addition of sulfonyl halide to olefins has been investigated for the conversion of olefins to vinyl sulfones.[6] However, these methods were limited by the availability of the starting materials prepared in the multistep sequences.

In the course of our studies on synthesizing vinyl sulfone using sulfone dianion,[7] we have directed attention to minimizing steps for the synthesis of α-methyl substituted vinyl sulfones utilizing 1,1-dilithiosulfone.[8] The dianion **2** of ethyl phenyl sulfone **1** which had been prepared by treating the sulfone with 2 equiv. of *n*-BuLi in THF at 0 °C was reacted with benzaldehyde to generate dianion intermediate **3**. After 30 min, tosyl chloride or diethyl chlorophosphate was added at –78 °C to the resulting dianion **3**, and the reaction mixture was warmed to room temperature to induce β-elimination reaction. The desired vinyl sulfone was obtained in low yield after usual work up and purification by chromatography (**Scheme 1**).



Scheme 1

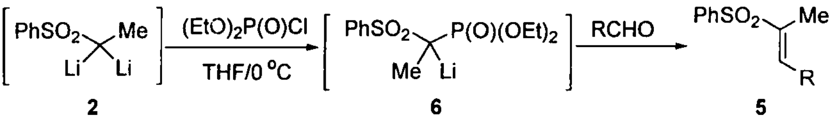
To compare with the preparation of vinyl sulfone *via* β-elimination reaction of intermediate **4**, we investigated Horner-Emmons olefination of α-sulfonyl phosphonate generated from 1,1-dilithiosulfone **2** in one-pot. As shown in **Scheme 2**, dianion **2** was reacted with diethyl chlorophosphate to generate phosphonate anion, subsequently reacted with bezaldehyde to give vinyl sulfone **5a** in 84% yield.

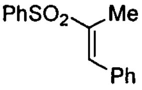
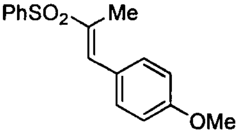
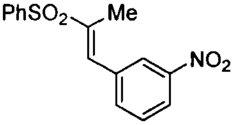
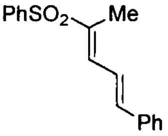
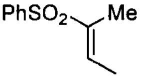


Scheme 2

We have a result that one-pot synthesis of α-methyl vinyl sulfone using 1,1-dilithiosulfone **2** *via* phosphonate is better than *via* lithiated β-hydroxy sulfone **3**. So we

Table 1. One-pot synthesis of vinyl sulfones from ethyl phenyl sulfones



entry	aldehyde	product (**5**)	yield(%)
a	PhCHO		84
b	*p*-MeO-PhCHO		75
c	*m*-NO_2-PhCHO		92
d	PhCH=CHCHO		94
e	CH_3CHO		52

decide to apply to various vinyl sulfone using one-pot Homer-Emmons reaction.[9] The dianion **2** of ethyl phenyl sulfone was prepared by treating the sulfone with 2 equiv. of *n*-BuLi in THF at 0 °C. After 30 min, diethyl chlorophosphate was added to the dianion **2** which led to the corresponding phosphorylated anion **6**, which reacted with various aldehydes to give the desired α-methyl vinyl sulfnes **5** in a good yield as shown in **Table 1**.

In correspondence with the general stereochemistry of the Homer-Emmons reaction, (E)-Vinyl sulfones are the exclusive products in the reaction of phosphorylated sulfone **6** with aldehyde. In case of enolizable carbonyl compounds, vinyl sulfone was obtained in a low yield (entry e, **Table 1**).

In summary, we have presented a convenient synthesis of vinyl sulfones from ethyl phenyl sulfone. This method provides a short route for the stereoselective transformation of ethyl phenyl sulfone into vinyl sulfone *via* 1,1-dilithiosulfone which is readily accessible.

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9. **General procedure for the synthesis of α-methyl vinyl sulfones *via* Horner-Emmons reaction**: A solution of ethyl phenyl sulfone (1 mmol) in 6mL of anhydrous THF was treated dropwise with a solution of 1.6 M *n*-BuLi (2 mmol) in hexane at 0°C.

After 30min of stirring at 0°C, the suspended reagent was treated dropwise with a solution of diethyl chlorophosphate (1 mmol) in 2 mL of THF. The reaction mixture was stirred for 30 min at 0°C. To the resulting yellow solution, aldehyde (1 mmol) was added and stirred for 1 hr at 0°C. Normal work-up was performed. The vinyl sulfone was purified by column chromatography on silica gel using EtOAc/ hexanes (1/9) as an eluent. ^{1}H NMR (200 MHz, $CDCl_3$) **5a** δ 2.23 (s, 3H), 7.37 (s, 5H), 7.40-7.59 (m, 3H), 7.60-8.0 (m, 3H); **5b** δ 2.09 (s, 3H), 3.80 (s, 3H), 6.90 (d, *J* = 8.77, 2H), 7.36 (d, *J* = 8.77, 2H) 7.47-7.60 (m, 3H), 7.74 (s, 1H), 7.88 (d, *J* = 5.5, 2H); **5c** δ 2.09 (s, 3H), 7.45-7.70 (m, 5H), 7.80 (s, 1H), 7.89 (d, *J* = 7.75, 2H), 8.14-8.18 (m, 2H); **5d** δ 1.91 (s, 3H), 6.70-6.90 (m, 2H), 7.20-7.26 (m, 3H), 7.30-7.52 (m, 6H), 7.76-7.81 (m, 2H); **5e** δ 1.71 (d, *J* = 7.0, 3H), 2.08 (s, 3H), 7.54-7.62 (m, 2H), 7.46-7.61 (m, 2H), 7.95-8.0(m, 2H).

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