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FACILE SYNTHESIS OF VINYL SULFONES FROM β-BROMO ALCOHOLS

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ABSTRACT: Vinyl sulfones are synthesized in good yields by dehydration of β -hydroxy sulfones derived from β -bromo alcohols.

The importance of vinyl sulfones in organic synthesis has been well established.¹ Much effort has been made to develop the preparation of vinyl sulfones. Our interest in this area has been focused towards the convenient preparation of vinyl sulfones.² In the course of investigation of the reactions of β -hydroxy sulfones,³ we have been interested in β -hydroxy sulfones as vinyl sulfone precursors.⁴ For the preparation of vinyl sulfones from β -hydroxy or β -halo sulfones, few reports are found in the literature.⁵ Recently, Brace reported a synthetic method for phenyl vinyl sulfone from thiophenol and 1, 2-dichloroethane.^{5d} If Brace's procedure were adapted to the synthesis of a few vinyl

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sulfones, more than 10 equivalents of 1,2-dichloro compounds would be required as starting materials, and some of these may not be readily available. We have studied the preparation of vinyl sulfones from β -hydroxy sulfones derived from β bromo alcohols.

	$\xrightarrow{R^1}$ PhS $\xrightarrow{R^1}$ ii)	PhSO₂ → OH
т Он R ²	T OH R ²	
1	2	3

Table 1. The preparation of β -hydroxy sulfone from β -bromo alcohols

reagents: i) aq. NaOH, PhSH at room temperature ii) Oxone in MeOH- water at 0 ^oC

entry	β-hydroxy sulfone 3	yield (%) ^a
а	PhSO ₂ OH	91
b	Me PhSO ₂ OH	88
с	HO PhSO ₂ OH	83
d	PhSO ₂ PhSO ₂ OH	85
e	PhSO ₂ OH PhSO ₂ OH	86

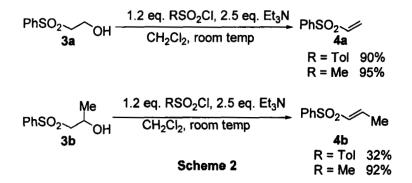
^a Isolated yield based on thiophenol

Initially, β -bromo alcohols 1 gave β -hydroxy sulfides 2 upon reaction with thiophenol and aqueous NaOH at room temperature. We obtained β -hydroxy sulfones 3 by the oxidation of the resulting β -hydroxy sulfides 2 with Oxone[®] in

methanol-water at 0 °C.⁶ The results of the preparation of β -hydroxy sulfones 3 from β -bromo alcohols 1 are summarized in Table 1. β -Hydroxy sulfones unlisted in Table 1 (entries 3f and 3g) were prepared from 2-phenylsulfonyl-1-ethanol 3a (Scheme 1).³

$$\begin{array}{cccc} PhSO_2 & & \hline OH & \hline i) \ 2.2 \ eq. \ n-BuLi/THF, \ -40 \ ^{\circ}C & PhSO_2 & OH \\ \hline ii) \ RBr, \ -40 \ ^{\circ}C \ to \ 0 \ ^{\circ}C & R \end{array} \\ \begin{array}{cccc} & & \mathbf{3f} & \mathbf{R} = \mathbf{benzyl} & 90\% \\ \mathbf{Scheme 1} & & \mathbf{3g} & \mathbf{R} = n-\mathbf{hexyl} & 87\% \end{array}$$

In a next stage, we have investigated one-pot dehydration of β -hydroxy sulfones 3 to generate vinyl sulfones 4. By treatment with TsCl and Et₃N in CH₂Cl₂ at room temperature, 2-phenylsulfonyl-1-ethanol 3a gave phenyl sulfonyl ethene 4a in 90% yield after 1 hour. In the case of 1-phenylsulfonyl-2-propene 3b, we obtained 32% (E)-1-phenylsulfonyl-2-propene 4b and recovered starting material under the same reaction conditions. This may result from the slow tosylation of secondary alcohols. When we used MsCl instead of TsCl, the corresponding vinyl sulfone was obtained in 92% yield (Scheme 2).



This optimized reaction condition was applied to synthesize various vinyl sulfones by the dehydration of β -hydroxy sulfones (**Table 2**).⁷

Pł	1SO₂~		SO ₂ Cl, 2.5 eq. Et ₃ N	PhSO₂→ R'
	2 ↑ R'		, room temp	Ŕ"
	3			4
	entry	β-hydroxy sulfor	ne vinyl sulfone (4)	yield (%) ^a
	а	PhSO ₂ OH	PhSO ₂	95
	b	Me PhSO ₂ OH	PhSO ₂ Me	92
	с	HO PhSO ₂ OH	PhSO ₂ Ms	90 ^{b, c}
	d	PhSO ₂ PhSO ₂ OH	PhSO ₂ SO ₂ Ph	95
	е	PhSO ₂ OH PhSO ₂ OH	PhSO ₂ PhSO ₂	94 ^b
	f	PhSO ₂ OH	PhSO ₂ Ph	95
	g	PhSO ₂ Hex	PhSO ₂ Hex	90

Table 2. The preparation of vinyl sulfones from β -hydroxy suolfones

 a Isolated yield. b 2.4 eq. of MsCl & 5 eq. Et_{3}N were used. c E/Z = 7 : 3

The advantage of this method lies in the convenient preparation of α methylene sulfones (entry **4a**, **4e**, **4f** and **4g** in **Table 2**), which have wide utility in organic synthesis. The preparations of α -methylene sulfones are not easy by aldol, Wittig, Peterson and related reactions, because formaldehyde would be necessary.

In summary, we have developed a facile method for the preparation of various vinyl sulfones from β -bromo alcohols. We obtained vinyl sulfones in good yields

by dehydration of β -hydroxy sulfones which had been prepared from β -bromo alcohols.

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- 7. General procedure for the preparation of vinyl sulfones from β-hydroxy sulfones: To a solution of β-hydroxy sulfones (1 mmol) and triethylamine (2.5 mmol) in dichloromethane (10 mL) was added slowly MsCl (1.2 mmol) at room temperature. The reaction mixture was stirred for 6 hours and then treated saturated ammonium chloride. The organic phase was extracted with dichloromethane (10 mL x 3), washed with water and brine. After removal of solvent, isolation of vinyl sulfone was readily accomplished by flash chromatography on silica gel. 25c ¹H NMR (200 MHz, CDCl₃) δ 2.93 (s, 3H, for trans: 2.99), 3.90 (d, J = 7.9, 2H, for trans: 3.72, J = 8.3), 5.05(dt, J = 7.9 and 6.2, for trans: 5.41, J = 8.3, and 12.3), 6.73 (d, J = 6.2, for trans: 6.52, J= 12.3), 7.50-7.67 (m, 3H), 7.80-7.89 (m, 2H); ¹³C NMR (50 MHz, CDCl₃) δ

38.0, 52.2, 103.2, 128.2, 129.3, 134.0, 140.2; **25d** ¹H NMR (200 MHz, CDCl₃) δ 3.81 (d, J = 7.8, 2H), 6.33 (d, J = 15.3, 1H), 6.72 (dt, J = 7.8 and 15.3, 1H), 7.32 - 7.76 (m, 10H); ¹³C NMR (50 MHz, CDCl₃) δ 57.4, 127.7, 128.0, 129.2, 129.3, 131.3, 133.8, 134.2, 137.4, 138.3, 139.1; **25e** ¹H NMR (200 MHz, CDCl₃) δ 6.80 (d, J = 14.2, 2H), 7.25 (d, J = 14.2, 2H), 7.58 - 7.70 (m, 6H), 7.87 - 7.92 (m, 4H); **25f** ¹H NMR (200 MHz, CDCl₃) δ 3.55 (s, 2H), 5.44 (s, 1H), 6.39 (s, 1H), 6.93 - 6.99 (m, 2H), 7.16 - 7.21 (m, 3H), 7.47 - 7.59 (m, 3H), 7.79 - 7.86 (m, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 35.5, 125.1, 126.9, 128.1, 128.5, 129.07, 129.09, 133.4, 135.7, 138.7, 150.6; **25g** ¹H NMR (200 MHz, CDCl₃) δ 0.77 (t, J = 5.8, 3H), 1.13 (m, 6H), 1.28 - 1.41 (m, 2H), 2.16 (t, J = 7.7, 2H), 5.67 (s, 1H), 6.30 (s, 1H), 7.40 - 7.65 (m, 3H), 7.70 - 7.84 (m, 2H).

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