

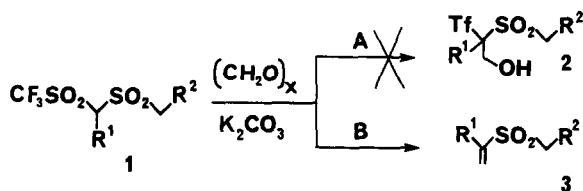
Mild Convenient Synthesis of α -Methylene Sulfones

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Summary: Reaction of paraformaldehyde with α -triflyl-sulfones and potassium carbonate at room temperature affords vinyl sulfones in good yield under mild conditions, with loss of triflate anion.

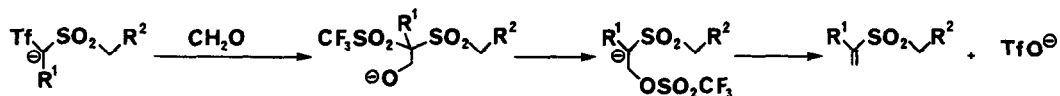
We wish to report a very mild and convenient synthesis of methylene sulfones using the mesyltriflone reagent **1**. As part of our ongoing study¹ to introduce various functional groups onto the methine position of a mono-alkylated mesyltriflone species, we attempted to prepare the hydroxy methylene compound **2** according to path A. (Tf = triflyl, CF_3SO_2^-).



Instead, however, the unexpected vinyl sulfones, **3**, were obtained in quantitative yield by path (B). A brief inspection of the literature reveals some related cases^{2,3}, shown here as **4** \rightarrow **5**.

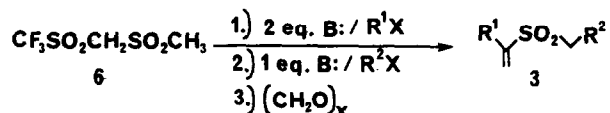


The mechanism, by comparison, may be explained by triflyl transfer from carbon to oxygen, followed by elimination of the triflate anion as follows:



Our synthetic procedure is extremely simple and provides high yields of vinyl sulfones, without tedious manipulation or the need for an aqueous work-up (low molecular weight sulfones are often appreciably soluble in water).

Vinyl sulfones are well known as useful intermediates for construction reactions⁴. Our present methodology offers several advantages over existing methods^{2,3,5} for their preparation, especially in light of the potential for the mesyltriflone reagent **6** to undergo several alkylations in one vessel.¹

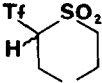



A natural extension of this methodology to include reaction with higher order aldehydes and ketones would provide a route to highly substituted vinyl sulfones. To date, this versatility has not been realized. The mesyl triflone anion is a very weak and hindered nucleophile ($\text{pK}_a \approx 4$) and no substituted vinyl sulfones were formed when reaction was attempted with either acetaldehyde, butyraldehyde, or benzaldehyde. Aldol condensations are a serious competing reaction in the case of the aliphatic aldehydes. The methylenation reaction that we have described is therefore limited to the very reactive and sterically accessible formaldehyde molecule.

GENERAL PROCEDURE: To a stirred THF solution of mesyltriflone **1** (1 mmol in 4 ml dry THF) was added finely ground, anhydrous potassium carbonate (1 mmol) and the resulting solution stirred at R.T., under nitrogen for 10 minutes. Paraformaldehyde (7 mmol) was added and stirring continued until TLC confirmed 100% conversion to product¹¹. The solution was then diluted with excess ether, suction filtered thru Celite, and the filtrate evaporated. The last traces of formaldehyde were removed, when necessary, by dissolving the residue in methylene chloride and passing down a silica plug. The yields were generally quantitative. Compounds **1a-1f** were synthesized according to a method described by us previously¹.

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Table I. Synthesis of Methylene Sulfones (3)

Entry	Triflyl Sulfone (1)	Product ^b Methylene Sulfone (3)	Vinyl Protons δ (PPM from TMS) ^{c,d}		Reference
			H _A :	H _B : ^f	
a	$\begin{array}{c} \text{CH}_3\text{CHSO}_2\text{CH}_3 \\ \\ \text{Tf}^a \end{array}$	$\begin{array}{c} \text{CH}_3\text{CSO}_2\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{H} \\ \quad \\ \text{A} \quad \text{B} \end{array}$	H _A : 5.70 ^e	H _B : ^f 6.15	3
b	$\begin{array}{c} \text{CH}_3\text{CHSO}_2\text{C}_2\text{H}_5 \\ \\ \text{Tf} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CSO}_2\text{C}_2\text{H}_5 \\ \\ \text{CH}_2 \end{array}$	5.85 ^e	6.15	6
c	$\begin{array}{c} \text{C}_5\text{H}_{11}\text{CHSO}_2\text{CH}_3 \\ \\ \text{Tf} \end{array}$	$\begin{array}{c} \text{C}_5\text{H}_{11}\text{CSO}_2\text{CH}_3 \\ \\ \text{CH}_2 \end{array}$	5.73 ^g	6.23	7
d	$\begin{array}{c} \text{C}_5\text{H}_{11}\text{CHSO}_2\text{C}_6\text{H}_{13} \\ \\ \text{Tf} \end{array}$	$\begin{array}{c} \text{C}_5\text{H}_{11}\text{CSO}_2\text{C}_6\text{H}_{13} \\ \\ \text{CH}_2 \end{array}$	5.75 ^g	6.20	8
e			5.60 ^g	6.04	9
f	$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CHSO}_2\text{CH}_3 \\ \\ \text{Tf} \end{array}$	$\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{CSO}_2\text{CH}_3 \\ \\ \text{CH}_2 \end{array}$	5.64 ^g	6.26	3

a) Tf = CF₃SO₂-; b) All compounds obtained gave satisfactory physical and spectral data; c) In CDCl₃; d) Assignments based on the known deshielding of vinyl proton (H_B) syn to the sulfonyl group in α,β -ethylenic sulfones¹⁰; e) Quartet, J=1.5 Hz; f) Broad singlet; g) Triplet, J=1.5 Hz.

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6. $^1\text{H-NMR}(\text{CDCl}_3)$: δ 1.33 (t, J=7Hz, 3H), 2.15 (bs, 3H), 2.97 (q, J=7Hz, 2H), 5.85(bs, 1H), 6.15(s, 1H); $\text{IR}(\text{CH}_2\text{Cl}_2)$: 1290, 1120, 950 cm^{-1} ; MS m/e=134.
7. $^1\text{H-NMR}(\text{CDCl}_3)$: δ 0.93(t, J=7Hz, 3H), 1.2-1.8(m, 6H), 2.43(bt, J=7Hz, 2H), 2.93(s, 3H), 5.73(t, J=2Hz, 1H), 6.23(s, 1H); $\text{IR}(\text{CH}_2\text{Cl}_2)$: 3035, 2952, 1296, 1170, 1120, 950, 780 cm^{-1} .
8. $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 149.04, 124.38, 52.26, 31.09, 31.04, 29.55, 27.90, 27.27, 22.21, 22.16, 22.06, 13.78; $\text{IR}(\text{CH}_2\text{Cl}_2)$: 2960, 2940, 2880, 2875, 1470, 1305, (s), 1125 (s), 960 cm^{-1} .
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11. Reaction time varied from an overnight period to 12 days, depending on substitution. Compound **1f** was the most sluggish to react.

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