A Direct and Efficient Synthesis of Allenyl Sulfones by the Horner-Wittig Reaction

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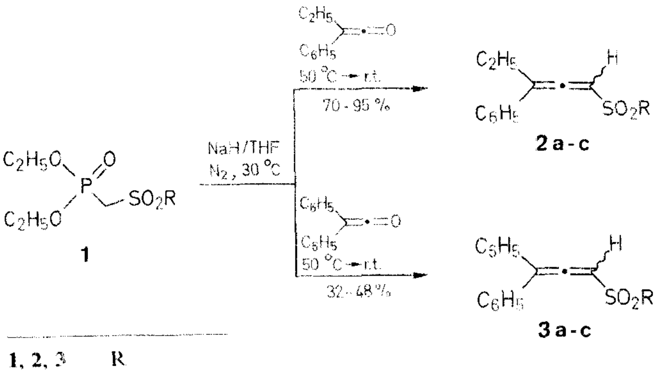
Allenic sulfones are directly prepared by the Horner-Wittig reaction of diethyl methyl(or aryl)sulfonylmethylphosphonate anions with ketenes. The method affords excellent to moderate yields respectively with phenylethyl and diphenylketene, the latter being more sensitive to basic media.

Allenic sulfones are compounds of potential biological interest. They can be obtained by isomerization of propargylic sulfones in basic media[1] or by oxidation of the corresponding sulfides[2] or sulfoxides.[3,4] However, these methods require the preparation of acetylenic or allenic intermediates. We have tried to find a one-step synthesis of allenylsulfones and have therefore investigated the preparation of allenic derivatives **2** and **3** by the Horner-Wittig reaction of sulfonylphosphonate anions with ketenes, since this method has already been successfully used in the direct synthesis of 1-alkenylsulfones.

We have found that diethylmethyl(or aryl)sulfonylmethylphosphonate anions (from **1**) undergo the Horner-Wittig reaction



1, 2, 3	R
a	CH_3
b	C_6H_5
c	p-ClC_6H_4

Table. 1-Methyl (or Aryl)sulfonyl-3-phenyl-1,2-pentadienes **2** and 1-Methyl(or Aryl)sulfonyl-3.3 diphenyl-1,2-propadienes **3**

Product	Yield[a] (%)	m.p. (°C)[b] (solvent)	Molecular Formula[c]	IR (KBr)[d] ν (cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS)[e] δ, J (Hz)
2a	95	72 (EtOAc/pentane)	$C_{12}H_{14}O_2S$ (222.3)	1940, 1300, 1135	1.2 (t, 3H); 2.6 (dq, 2H, J = 3); 3 (s, 3H); 6,6 (dd, 1H, J = 3); 7,4 (m, 5H)
2b	70	62 (PE)[f]	$C_{17}H_{16}O_2S$ (284.4)	1940, 1300, 1130	1.1 (t, 3H); 3 (dq, 2H, J = 3); 6.6 (dd, 1H, J = 3); 7.3–7.9 (m, 10H)
2c	80	96 (EtOAc/pentane)	$C_{17}H_{15}ClO_2S$ (318.8)	1940, 1310, 1150	1.1 (t, 3H); 2.5 (dq, 2H, J = 3); 6.5 (dd, 1H, J = 3); 7.2 (s, 5H); 7.4, 7.7 (q, 4H)
3a	48	162 (EtOAc/pentane)	$C_{16}H_{14}O_2S$ (270.3)	1940, 1300, 1130	3 (s, 3H); 6.7 (s, 1H); 7.4 (s, 10H)
3b	32	58 (PE)[f]	$C_{21}H_{16}O_2S$ (332.4)	1940, 1295, 1130	6,65 (s, 1H); 7.1–7.9 (m, 15H)
3c	40	100 (EtOAc/pentane)	$C_{21}H_{15}ClO_2S$ (366.8)	1945, 1325, 1155, 1145	6.65 (s, 1H); 7.3 (m, 10H); 7.4, 7.7 (q, 4H)

[a] Yield of isolated pure product based on **1**.

[b] Uncorrected, measured with a Gallenkamp apparatus.

[c] Satisfactory microanalysis obtained: C ±0.21, H ±0.12, Cl ±0.30, S ±0.20.

[d] Recorded on a Perkin-Elmer 1310 Infrared spectrophotometer.

[e] Recorded on a Bruker WP 100 spectrometer.

[f] PE = petroleum ether.

with both arylalkyl and diarylketenes.[5] We now describe the reaction of these anions with ethylphenylketene and diarylketene.

The method affords high yields when ethylphenylketene is used. The yields are lower with diphenylketene which is sensitive to basic media. Thus, allenic sulfones **3** are isolated in moderate yields only when no excess of sodium hydride is employed.

1-Methyl(or Aryl)sulfonyl-3-phenyl-1,2-pentadienes 2; General Procedure:

A 80% sodium hydride dispersion in mineral oil (70 mg, ~ 2.3 mmol) is washed three times by decantation with anhydrous pentane and is resuspended in dry THF (5 mL). A solution of phosphonic ester **1**[6,7] (2 mmol) in THF (10 mL) is added under nitrogen by syringe. Hydrogen is evolved and the mixture is kept at 30 °C in a waterbath for 30 min. Then, freshly distilled ethylphenylketene[8] (2.2 mmol) in THF (5 mL) is added dropwise over 10 min. When the addition is complete, the mixture is warmed at 50 °C for 10 min, and allowed to stand at room temperature for 30 min. The mixture is then poured into cold water (20 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The organic layers are combined, washed with H_2O, dried (Na_2SO_4), and evaporated under vacuum. Product **2a** is purified by recrystallization from EtOAc/pentane. Products **2b** and **2c** are chromatographed on silica gel using EtOAc/hexane (3:7) as eluent.

1-Methyl(or Aryl)sulfonyl-3,3-diphenyl-1,2-propadienes 3: General Procedure:

An 80% sodium hydride dispersion in mineral oil (30 mg ~ 1 mmol) is treated as described above with a solution of phosphonic ester **1** (1 mmol). The Freshly distilled diarylketene[9] (1.1 mmol) is added in the same manner. After work-up, compounds **3** are purified by column chromatography on silica gel using CH_2Cl_2/hexane (1 : 1) as eluent.

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