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Synthesis of Enantiomerically Pure 4-Substituted (1Z, 3E) -1 [(R)-p-Tolylsulfinyl]-2-t-Butyldimethylsilyloxy-1,3-Butadienes.

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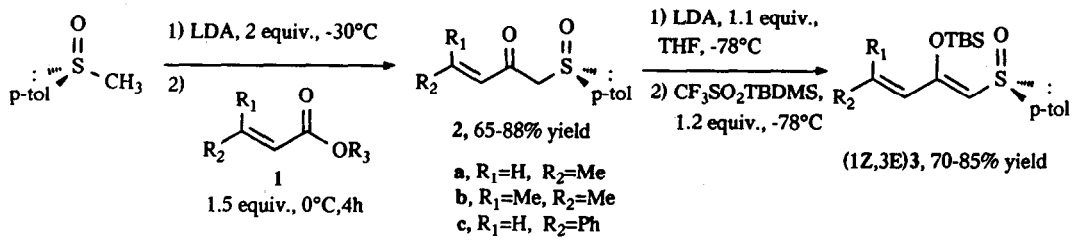
Abstract: *The synthesis of enantiomerically pure 4-substituted (1Z,3E) 1-[(R)-p-tolylsulfinyl]-2-t-butyldimethylsilyloxy-1,3-butadienes from allylic β-ketosulfoxides is described.*

Although optically active sulfinyl dienophiles have been shown to give good asymmetric induction in Diels-Alder cycloaddition[1,2,3], very little has been done with sulfinyl dienes which have been used, till now, in racemic form[4-7], due to the lack of methods to synthesize the enantiomerically pure derivatives.

However, the good diastereoselectivity reported in the literature[4-7] with racemic sulfinyl dienes, prompted us to develop good ways to synthesize these molecules in optically active form.

We recently reported[8] a first method to obtain enantiomerically pure 4-alkyl (or 4-aryl) (1E, 3E) 1-p-tolylsulfinyl-1,3-dienes. We describe now the synthesis of enantiomerically pure 4-substituted (1Z, 3E)-1-[(R)-p-tolylsulfinyl]-2-t-butyldimethylsilyloxy-1,3-butadienes, the heteroatom on C-2 being of considerable interest to prepare highly functionalized ring systems[9] and to control the regioselectivity of the cycloaddition.



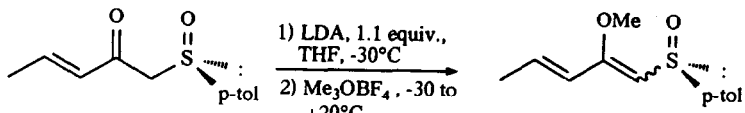
Condensation of (+)(R) methyl p-tolylsulfoxide[10] to the α, β-unsaturated esters 1 in presence of LDA afforded in good yields the corresponding unsaturated β-ketosulfoxides 2, characterized in ^{1}H NMR by the vinylic proton (around 6 ppm) and the AB pattern for the methylene α to the sulfoxide (around 4 ppm). Enolization of the carbonyl group was carried out with LDA and the resulting enolate quenched with t-butyldimethylsilyl triflate to give a 90/10 mixture of (1Z, 3E) and (1E, 3E) dienes 3, easily determined by NMR from the vinylic hydrogen α to sulfoxide (around 5.5 ppm).
The pure (1Z, 3E) diene 3[11] was easily obtained by flash chromatography. The stereochemistry was attributed by NMR from NOE experiments : irradiation of the vinylic proton H-1 lead to a clear NOE on H-3.

Table I: β-ketosulfoxides 2 and sulfinyldienes 3

	R_1	R_2	R_3	Yield % 2	$[\alpha]_D$[a] 2	Yield %[b] (1Z,3E)3	$[\alpha]_D$[c] (1Z,3E)3
a	H	Me	Me	65	+241	85	-201[d]
b	Me	Me	Et	88	+278	70	-119[e]
c	H	Ph	Me	85	+174	70	-118[f]

a) isolated yields, b)$CHCl_3$, c=1, c) $CHCl_3$, d) c=1.8, e) c=0.5, f) c=1.3

It was also attempted to quench the enolate with an alkyl instead a silyl. This was carried out from the lithium enolate of the β-ketosulfoxide **2a** and trimethyloxonium tetrafluorobotate as a quenching agent. The enol ether was obtained in 75% yield as a 84/16 mixture of (1Z, 3E/1E,3E) isomeric dienes **4**, determined by NMR from the vinylic proton H-1 (5.5 ppm in the ZE isomer and 5.4 in the EE) and from the methoxy group (3.9 and 3.6 ppm respectively).



2a

4, 75% yield, EZ/EE=84/16

However the separation of these two isomers was impossible by chromatography.

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11) Typical exemple of ^1H NMR of sulfinyl diene: 1Z,3E **3a** (200 MHz,$CDCl_3$): δ : 0.3 and 0.4 (2s, 6H, Me_2Si), 1.1 (s, 9H, t-BuSi), 1.8 (dd, J=7 Hz, 3H, CH_3), 2.4 (s, 3H, CH_3-Ar), 5.6 (s,1H, H-2), 5.9 (qd, 1H, H-4, $J_{4,5}$=15 Hz, $J_{4,6}$=1Hz), 6.1 (qd, 1H, H-5, $J_{5,6}$=7 Hz, $J_{5,4}$=15 Hz), 7.5-7.3 (AA'BB', 4H, J=8 Hz, arom.).

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