## First Syntheses of Chiral 2-Sulfinylbutadienes

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Abstract: The title compounds were readily prepared respectively from (S)-3-p-tolylsulfinylbut-3-en-2-ol 3 and (S)-3-p-tolylsulfinylbut-3-en-2-on 4.

To date, asymmetry in the Diels-Alder reaction has been mainly introduced through chiral dienophiles and only relatively few examples are known where chirality is brought by the diene counterpart.<sup>1</sup>

To the best of our knowledge, among the various chiral groups borne by the diene, only three examples are known where this group is a sulfoxide.<sup>2-5</sup> It is worthy to note that in all these instances, the sulfoxide group is on the first carbon atom of the dienic system.

We wish to report here our preliminary results concerning the synthesis of the first chiral 2-sulfinylbutadienes 1 and 2: (R)-p-tolylsulfinyl-1,3-butadiene and (S)-p-tolylsulfinyl-3-trimethylsilyloxy-1,3-butadiene.



We recently described <sup>6</sup> very easy access to both chiral alcohol **3** and ketone **4** which seemed to be interesting precursors of the desired optically active dienes. The parent compound of this family was very easily obtained starting with allylic alcohol **3**, synthesized from (R)-2-ethoxyethyl-p-tolylsulfoxide as a mixture of diastereoisomers.



Reaction of alcohol 3 with methanesulfonyl chloride  $(CH_2Cl_2, 0^{\circ}C)$  afforded the stable<sup>7</sup> mesylate 5 in 93% yield, as a colorless oil. Subsequent treatment of 5 with DABCO (2 eq.,  $CH_2Cl_2$ , reflux) yielded the title product 1 (62% yield after crystallization).<sup>8</sup> The remarkable stability of diene 1 allowed its purification through liquid chromatography (cyclohexane : ether 7:3), its analysis by GC and its storage for several days at 20°C without degradation.<sup>9</sup>

On the other hand, various attempts to convert ketone 4 into dienes via Wittig reactions proved to be unsuccessful. This unsaturated  $\beta$ -ketosulfoxide 4 was however readily transformed into the silyloxysulfinylbutadiene 2 via treatment of its enolate (Et<sub>3</sub>N) by trimethylsilylchloride. The sensitivity of this diene towards hydrolysis make its purification difficult.<sup>10</sup>



These syntheses offer an easy access to simple but hitherto unknown chiral 2-sulfinyl substituted butadienes. We are currently investigating the generalization of this methodology to other dienes and their reactivity in Diels-Alder reactions.<sup>11</sup>

## **References and Notes**

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- 8. 1: m.p. = 39-40°C (pentane-ether). H<sup>1</sup>- NMR (400 MHz)  $\delta$ (CDCl<sub>3</sub>/TMS) : 2.39 (s, 3H, ArCH<sub>3</sub>) ; 5.22 (d, 1H, part A of AMX, J<sub>AX</sub> = 0, J<sub>AM</sub> = 11.3 Hz) ; 5.48 (d, 1H, part X of AMX, J<sub>AX</sub> = 0, J<sub>MX</sub> = 17.7 Hz) ; 5.86 (s, 1Hy) ; 6.14 (s, 1Hz) ; 6.24 (dd, part M of AMX, J<sub>AM</sub> = 11.3 Hz, J<sub>MX</sub> = 17.7 Hz) ; 7.26-7.56 (AA'BB' H<sub>M</sub> system, 4 H arom).  $\lambda$  max (EtOH) 231 nm ( $\epsilon$  14200).
- 9. This is in striking contrast with Hoffmann's sulfonyldienes which quickly dimerize at room temperature : Hoffmann, H.M.R. ; Weichert, A. ; Slawin, A.M.Z.; Williams, D.J. Tetrahedron, 1990, 46, 5591.
- 10. **2** : Crude yield = 51%.  $H^1$  NMR (400 MHz)  $\delta$ (CDCl<sub>3</sub> /TMS) : 0.15 (s, 9H, (C<u>H</u><sub>3</sub>)Si) ; 2.38 (s, 3H, ArC<u>H</u><sub>3</sub>) ; 4.38 (d, 1Hc or d, Jcd = 2.2 Hz) ; 4.65 (d, He pToIS(O) or d, Jcd = 2.2 Hz); 6.11 (s, 1 Ha or b); 6.21(s, 1 Ha or b); 7.27-7.56 (AA'BB' system, 4 Harom). Small amounts of 4 were observed in the N.M.R. spectrum of crude 2.



11. Preliminary studies showed a high reactivity of diene 1 towards maleic anhydride at 20°C.

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