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CONJUGATE ADDITIONS OF HETEROANIONS TO ETHYNYL p-TOLYL (+)-(R)-SULFOXIDE

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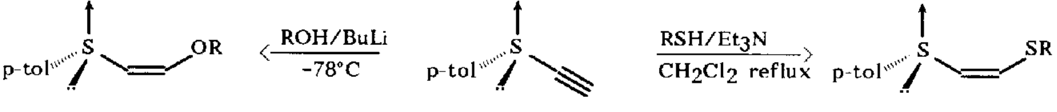
***Summary** : Conjugate additions of several heteroanions (thiolates, alkoxides, phenoxides) to ethynyl p-tolyl (+)-(R)-sulfoxide 1 proceed stereospecifically to give only (Z) isomers of 2-alkylthio- or alkoxy-(R)-vinylsulfoxides.*

In recent years, chiral α,β-acetylenic sulfoxides easily obtained by the Andersen procedure from l-menthyl (-)-(S)-p-toluene sulfinate have been used in some asymetric syntheses[1] ;

We recently reported that (+)-(R)-ethynyl p-tolylsulfoxide **1** is a good chiral dienophile in cycloaddition reactions[2] and could serve as masked chiral ketene equivalent.[3] On the other hand, stereoselective reduction of chiral acetylenic sulfoxides with LAH or catalytic hydrogenation give 1-alkenyl-p-tolyl (+)-(R)-sulfoxides (E) and (Z) respectively,[4] used in the synthesis of lignan lactones.[5]

Pursuing our study of the chemistry of α,β-unsatured sulfoxides, we report here our preliminary results utilizing **1** as a Michael acceptor. Several types of optically pure β-hetero-substitued ethylenic sulfoxides can be easily obtained in this way (Scheme 1).



3 **1** **2**

Some illustrative examples are shown in Table 1.

In the case of heteroanions derived from sulfides **2a-c** the chiral ethynyl sulfoxide **1** (5 mmol) was treated directly with thiols (6 mmol of CH_3CH_2SH, C_6H_5SH or $CH_2=CH-CH_2SH$) in CH_2Cl_2 at 35°C and three drops of Et_3N as a base. For **2b** similar results were obtained when using n-BuLi in THF at -78°C to generate the thiolate. The reaction was quenched with saturated aqueous NH_4Cl at 0°C.

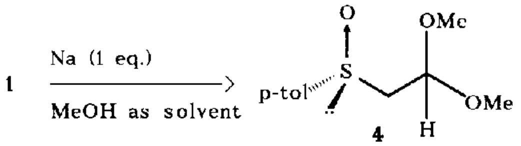
Table 1.

$-XR$	Product	Isolated yield[a] (%)	$[\alpha]_D$, deg (c)[b]
$-SCH_2CH_3$	**2a**	65	-520 (1)
$-SC_6H_5$	**2b**[c]	76	-485 (1)
$-SC_6H_5$	**2b**[d]	89	-490 (1)
$-SCH_2CH{=}CH_2$	**2c**	51	-407 (0,5)
$-OCH_3$	**3a**[e]	77	-421 (1)
$-OCH_2CH{=}CH_2$	**3b**	66	-300 (2,5)
$-OC_6H_5$	**3c**	50	-194 (1)

[a] **2a-c** were purified by column chromatography (silica gel), **3a** by recrystallization, mp = 55°C (C_5H_{12}) and **3b-c** by preparative layer chromatography. [b] Measured for solution in acetone at 20°C. [c] **2b** is crystallised : mp = 62°C (ether). [d] In THF with n-BuLi at -78°C. [e] The optical purity of this compound has been determined by ^1H-NMR using $Eu(hfc)_3$ as chiral shift reagent.

Treatment of **1** with alkoxides (CH_3OH or $CH_2{=}CH{-}CH_2OH$ with 1 eq. of n-BuLi) or phenoxides at -78°C to -20°C followed by hydrolysis of the resulting adducts (NH_4Cl sat., 0°C) proceeded well to give a single adduct of the alkoxysulfoxide.[6]

It is noticeable that the double addition product, optically active α-sulfinylacetaldehyde acetal **4**[7] is readily obtained by treatment of **1** with 1 eq. of Na in MeOH at 25°C.



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All of these reactions afforded (Z) alkenylsulfoxides in high yield. The (E) stereoisomers could not be detected from the analysis of NMR spectra. The (Z) geometry of the double bond was unambiguously confirmed by the coupling constant of the olefinic proton (J_{A-B} = 9 Hz for compounds **2** and J_{A-B} = 6 Hz for **3**).

In summary, all of these Michael additions proceed stereospecifically to give (Z) adducts which is in striking contrast with the cis addition of cuprates.[8]

Full detail, extension of these results to other heteroanions and utilisation of these very useful chiral β-heterosubstitued sulfoxides **2**, **3**, **4** will be reported in due course.

References and Notes

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6. Action of t-BuO^-Li^+ led to the degradation of **1**.
7. **4** Yield : 91% ; colourless oil ; $[\alpha]_D$ +170 (c 1, propanone) : ^1H-NMR (90 MHz) $\delta(CDCl_3)$: 7.70-7.43 (4H, dd) ; 4.85 (1H, dd, J = 4.5 and 6.8 Hz) ; 3.5 (3H, s) ; 3.4 (3H, s) ; 3.20 (1H, dd, J = 4.5 and 14 Hz) ; 3 (1H, dd, J = 6.8 and 14 Hz) ; 2.45 (3H, s).
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