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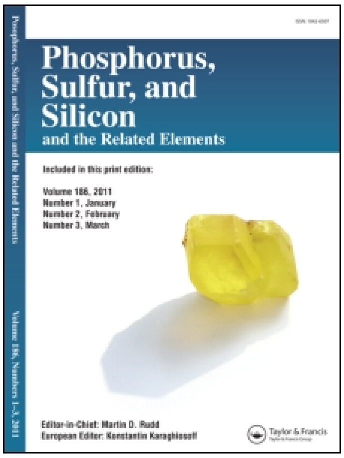

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Remote Asymmetric Induction by Sulfoxides: DIBAL Reduction and Et_2AlCN Hydrocyanation of *ortho*-(*p*-Tolylsulfinyl)Benzyl Ketones

José L. García Ruano[a]; M. Mercedes Rodríguez-Fernández[a]; M. Ángeles Fernández-Ibáñez[a]; M. Carmen Maestro[a]
[a] Departamento de Química Orgánica, Universidad Autónoma de Madrid, Madrid, Spain

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M. Carmen Maestro
Departamento de Química Orgánica, Universidad Autónoma de Madrid, Madrid, Spain

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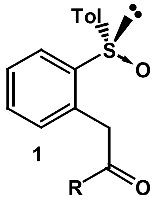
The efficiency of the sulfinyl group as an element of remote control of the stereoselectivity (1,5-asymmetric induction) in the DIBAL reduction and Et_2AlCN hydrocyanation of the carbonyl group in unsubstituted *ortho*-*p*-tolylsulfinylbenzyl ketones **1** has been evaluated with and without stoichiometric amounts of $Yb(OTf)_3$ as Lewis acid, as well as its α-methyl derivatives **2a** and **2b**, with the aim of establishing the influence of an additional stereogenic center on the stereoselectivity.

Synthesis of ketosulfoxides **1** has been attained by condensation of (S)-2-(*p*-tolylsulfinyl)benzyllithium with esters. On the other hand, the α-methyl-substituted compounds **2** have been obtained by two different procedures: a) methylation of **1** with NaH/MeI to afford **2a** and **2b** as an approximately 1:1 epimeric mixture at the benzylic position and b) by oxidation with PCC of the alcohols (epimeric mixtures at the hydroxylic carbon) obtained from reactions of aldehydes with the lithium carbanion derived from (S)-2-(*p*-tolylsulfinyl)ethylbenzene.[1]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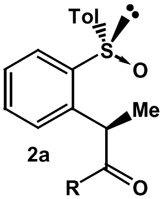
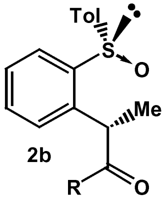

2a


2b

R = H, Me, *n*-Pr, *i*-Pr, Ph

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Address correspondence to M. Mercedes Rodríguez-Fernández, Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain. E-mail: mercedes.rodriguez@uam.es

The new stereogenic center with *R* configuration at the benzylic position does not change the sense of the sulfur induction. In the presence of Yb(OTf)$_3$, both reactions are highly stereoselective, favoring the nucleophilic attack by the less hindered face of the presumed ytterbium chelate (*(S)-alcohol*: 94% de ⇔ from **1**; R = Me and >98% de ⇔ from **2a**; R = Me. *(S)-cyanohydrin*: >98% de from **1**or **2a**). Both substrates show a low selectivity in the absence of the Lewis acid.

On the contrary, the ketone **2b** (*S* configuration) provides a nonselective behavior in the presence of Yb(OTf)$_3$, (*(S)-alcohol*: 12% de; *(S)-cyanohydrin*: 40% de ⇔ R=Me), however, a high induction in hydrocyanation reaction is attained without the Lewis acid (*(S)-alcohol*: 16% de; *(R)-cyanohydrin*: >98% de ⇔ R=Me). The selectivity of the reactions with Et$_2$AlCN is notably influenced by the thermodynamic stability of the cyanohydrins, prone to equilibration, especially in the presence of the Lewis acid and with a significant influence of the stereoelectronic nature of the R group.

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