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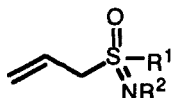
DIASTEREOSELECTIVE REACTIONS OF ALLYLIC SULFOXIMINE ANIONS

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Abstract The conjugate addition reactions of lithiated *N*-*p*-tolyl *S*-phenyl *S*-2-propenyl sulfoximine (4) with cyclic and acyclic enones gives exclusively 1,4- α adducts, the reactions with acyclic enones are highly diastereoselective.

In contrast to the chemistry of allylic sulfoxides and sulfones relatively little is known about the chemistry of allylic sulfoximines.¹ In 1979, Johnson² disclosed the synthesis of the first reported allylic sulfoximine. The synthesis of enantiomerically pure allylic sulfoximines has been recently reported,^{3,4} and Gais has demonstrated they undergo S_N2 or S_N2' like displacement reactions with homocuprates.³ In 1991 Harmata⁵ reported that the reaction of lithiated (1) with either 2-cyclopentenone or 2-cyclohexenone gave mixtures in which the 1,4- α adducts were slightly favoured over the 1,4- γ adducts. More recently we have reported that the conjugate addition reactions of lithiated (3) with cyclic and acyclic Michael acceptors gives mainly 1,4- γ and 1,4- α adducts respectively in THF and 1,4- α and 1,4- γ adducts respectively in HMPA/THF.⁶ Although the 1,4- γ adducts from cyclic enones could be isolated in high diastereomeric purity, these reactions proceeded with modest regioselectivity with respect to α versus γ attack on the lithiated sulfoximine. Furthermore acyclic enones gave products from 1,2 and 1,4 addition of lithiated (3).



- (1), $R^1 = p\text{-Tol}$, $R^2 = \text{Ph}$
- (2), $R^1 = \text{Ph}$, $R^2 = \text{H}$
- (3), $R^1 = \text{Ph}$, $R^2 = \text{SiBu}^t\text{Ph}_2$
- (4), $R^1 = \text{Ph}$, $R^2 = p\text{-Tosyl}$

In this lecture I report the stereochemistry and diastereoselectivity of the conjugate addition reactions of lithiated *N*-*p*-tolyl *S*-phenyl *S*-2-propenyl sulfoximine (4) with enones. The results of these investigations are summarized in the Table.

In contrast to the chemistry reported for lithiated (1)⁵ and (3)⁶, lithiated (4) gave exclusively 1,4- α adducts with both cyclic and acyclic enones.⁷ Interestingly the regiochemistry of the reaction of lithiated (4) with enones is also different to that of lithiated allyl phenyl sulfone which gives exclusive 1,4- γ adducts with cyclic enones and 1,4- α adducts with acyclic enones.⁸

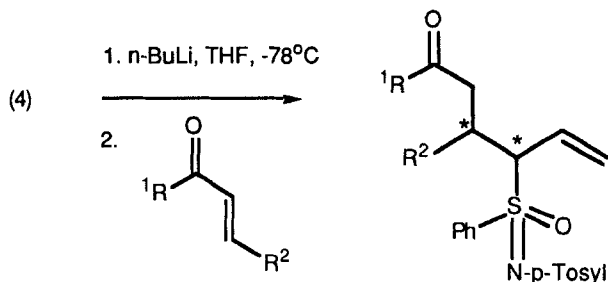


TABLE. Conjugate addition reactions of lithiated **4** with enones.

Entry	R ¹	Enone R ²	Diastereomeric ratio	Yield (%)
1		-(CH ₂) ₂ -	49 : 33 : 10 : 8	87
2		-(CH ₂) ₃ -	47 : 25 : 14 : 14	92
3	Ph	Ph	93 : 7	90
4	Me	Ph	90 : 10	45
5	Ph	Me	94 : 6	61
6	Me	Me	84 : 16	71

The application of these reagents to the asymmetric synthesis of chiral acyclic molecules is currently under active investigation.

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