

[A0038]

NUCLEOPHILIC ADDITIONS TO 10-ISOBORNYLSULFINIMINES

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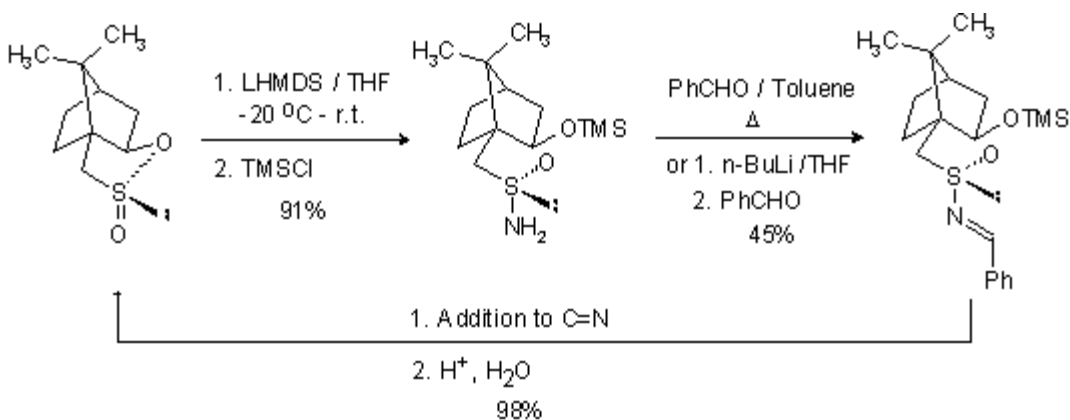
1. INTRODUCTION

Optically active sulfinimines proved to be versatile chiral auxiliaries in the synthesis of amino-compounds. In this presentation new camphor derived sulfinimine is described, as well as its reactions with some nucleophiles. Lewis acid catalyzed additions of ketene silyl acetal to sulfinimine is presented and hetero Diels-Alder reaction with Brassard's diene. As opposed to majority of sulfur containing chiral auxiliaries, title compound may be recycled without loss of optical purity.

2. SYNTHESIS OF (S_S)-10-ISOBORNYLSULFINIMINE.

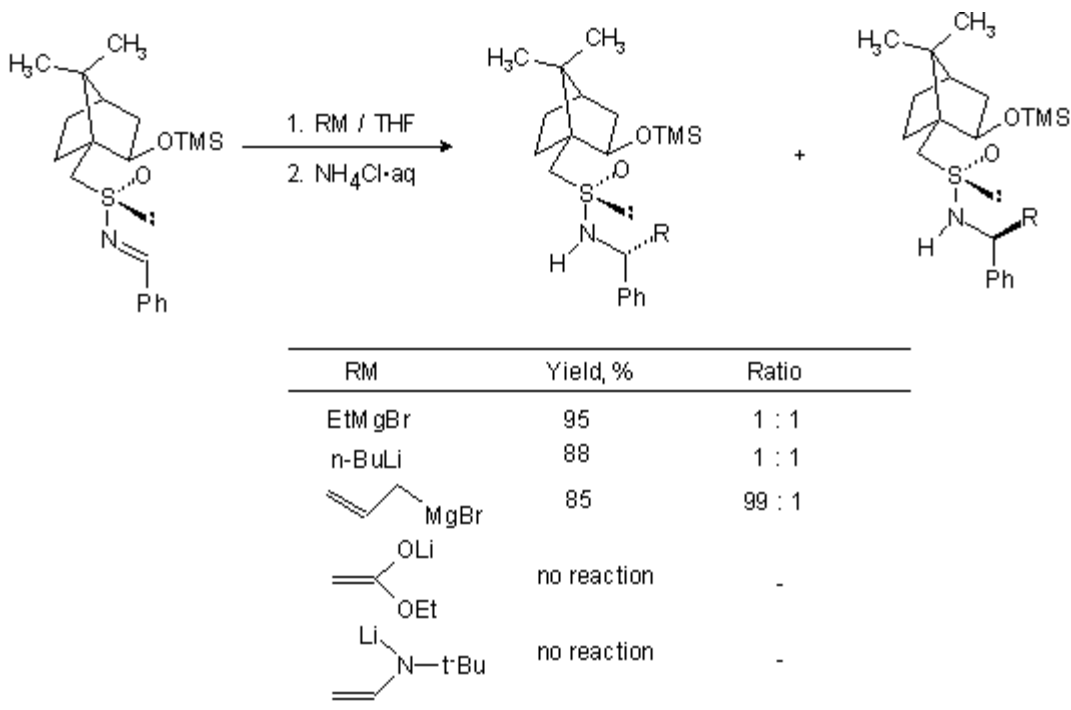
The reaction of 10-isobornylsulfinate (Kawecki R., Urbanczyk- Lipkowska Z. *Synthesis* **1996**, 603) with LHMDS provides sulfinamide in good yield. Subsequent condensation with aromatic aldehyde gives sulfinimine which after nucleophilic addition can be converted to initial sulfinate by acid treatment (scheme 1. lower arrow).

Scheme.1



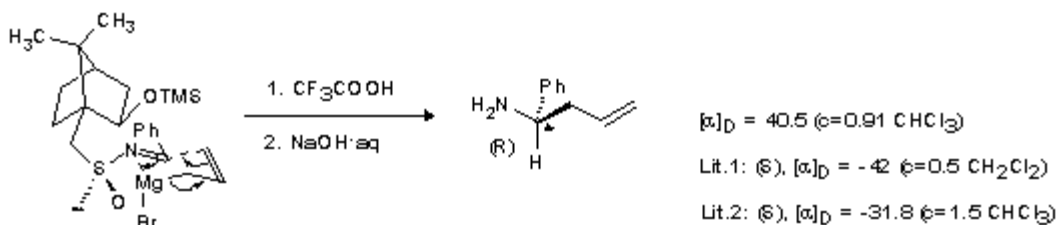
3. ADDITIONS OF ORGANOMETALLIC REAGENTS.

Scheme 2.



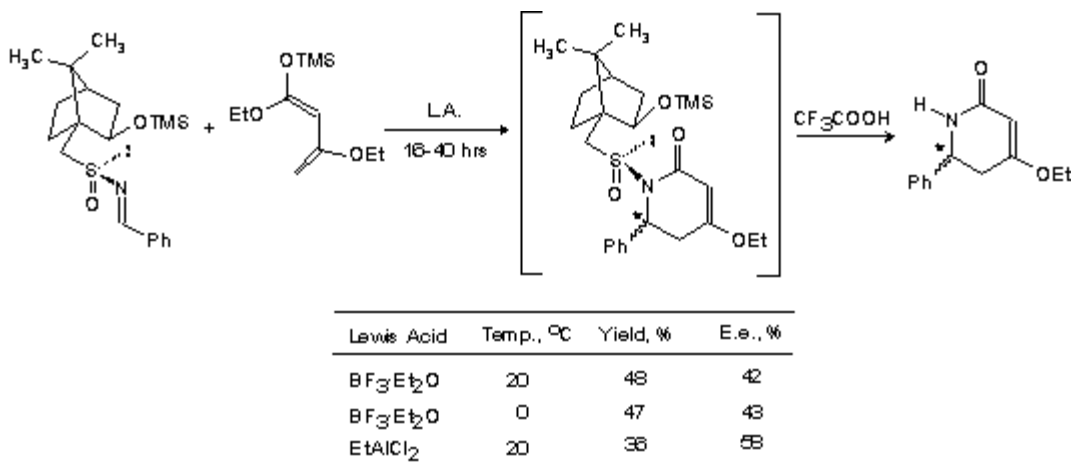
Addition of organolithium or Grignard reagents to C=N bond is not stereoselective. One exception is allylmagnesium bromide, which undergoes reaction through six-membered ring transition state (scheme 3), affording exclusively one diastereoisomer.

Scheme 3.



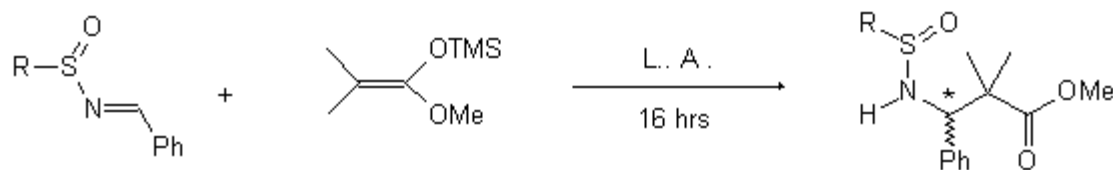
4. LEWIS ACID CATALYZED CYCLOADDITION TO 10-ISOBORNYLSULFINIMINE.

Scheme 4.



5. LEWIS ACID CATALYZED ADDITION OF KETENE SILYL ACETAL TO SULFINIMINES.

Scheme 5.



RS(O)	Lewis Acid (eq.)	Solvent	Temp., °C	Unreacted sulfinimine, %	Yield of product, %	D.e., %
(±)-p-TolS(O)	BF ₃ ·Et ₂ O (1.3)	CH ₂ Cl ₂	20	27	53	61
	BF ₃ ·Et ₂ O (1.1)	CH ₂ Cl ₂	-70	74	9	34
	BF ₃ ·Et ₂ O (1.1)	CH ₃ CN	20	47	35	42
	Et ₂ AlCl (1.1)	CH ₂ Cl ₂	20	46	28	47
	EtAlCl ₂ (1.1)	CH ₂ Cl ₂	20	38	39	60
	SnCl ₄ (1.1)	CH ₂ Cl ₂	20	45	13	47
	Yb(OTf) ₃ (0.5)	CH ₂ Cl ₂	20	59	19	61
	Yb(OTf) ₃ (0.5)	CH ₃ CN	20	61	17	26*
	TrSbCl ₆ (0.14)	CH ₂ Cl ₂	-70	67	14	40*
	BF ₃ ·Et ₂ O (1.1)	CH ₂ Cl ₂	20	42	0	-
	EtAlCl ₂ (1.1)	CH ₂ Cl ₂	20	78	0	-

* D.e. of the second diastereoisomer

6. CONCLUSIONS.

Above results show that 10-isobornylsulfinimine is rather poor electrophile in reactions with enolates and azaenolates. Similar situation occurs in the case of Mukaiyama type condensation, despite simple p-tolylsulfinimine reacts smoothly with medium stereoselectivity. The use of 10-isobornylsulfinimine as dienophiles in hetero Diels-Alder reaction seems to be the most promising.

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Comments

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