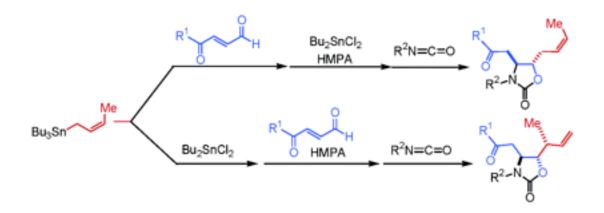
One-Pot Synthesis of Nitrogen Heterocycles Initiated by Regioand Diastereoselective Carbon-Carbon Bond Formation of Bifunctional Carbonyl Compounds



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Tin-Oxygen Bond

Allylic Stannanes add to Aldehdes:

Allenic Stannanes add to Aldehydes:

$$R_1$$
 R_1 R_2 R_3 R_4 R_4 R_4 R_5 R_4 R_5 R_4 R_5 R_5

Propargylic Stannanes add to Aldehydes:

Nucleophilicity of Tin-Oxygen Bond

$$R \downarrow O \downarrow H \longrightarrow R \downarrow O - Sn \longrightarrow R \downarrow$$

- 1. L.A. can't be used because the stability of compound 1
- 2. Tributyltin system does't work without the help of L.A.
- 3. Allylic chloro-dibutyltin system works well with high chemoselectivity

One-Pot Synthesis of 2-Oxazolidinones

R1 CHO
$$\frac{Sn}{2}$$
, HMPA $\frac{R^2N=C=O}{O^{\circ}C, 1 \text{ h}}$ $\frac{R^2$

entry	R^1	\mathbb{R}^2	Sn (2)	Product and yield/ %
1	n-C ₈ H ₁₇	Ph	$Bu_3Sn(2a)$	No reaction
2			$Bu_2ClSn(2b)$	4a 99% ^b
3			2 b	3a 81% (trans: cis = 91 : 9)
4	p-ClC ₆ H ₄ (1b)	Ts	2b	3b 54% (trans: cis = 100 : 1)

^a**1**, 1mmol; **2**, 1 mmol; HMPA, 1 mmol; R²NCO, 1mmol; THF, 1mL. ^b Without HMPA

The trans Selectivity

$$R^2$$
 R^2 R^2

The Application of Crotyltin Reagents

Generated Allylictins A as Nucleophiles

Bu₂SnCl₂
HMPA R²N=C=O

THF, 60 °C, 3 h 0 °C, 1 h 60 °C, 0.5 h R²-N O

R¹=
$$n$$
-C₈H₁₇ (1a) R²= Ts 5a 62% (ds = 100%)

R¹= n -C₈H₁₇ (1a) R²= n -C₄H₉ 5b 75% (ds = 100%)

R¹= p -ClC₆H₄ (1b) R²= Ts 5c 70% (ds = 100%)

Mechanism of Generated Allylictins A as Nucleophiles

Generated Allylictins B as Nucleophiles

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Mechanism of Generated Allylictins B as Nucleophiles

Conclusion

A one-pot synthesis of nitrogen heterocyclic compounds was initiated by chemoselective allylation.

Regio- and diastereoselective carbon-carbon bond formation was established in the side chain of the rings.