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Highly Diastereoselective Samarium-Reformatsky Reaction of Chiral α-Bromoacetyl-2-oxazolidinones with Aldehydes

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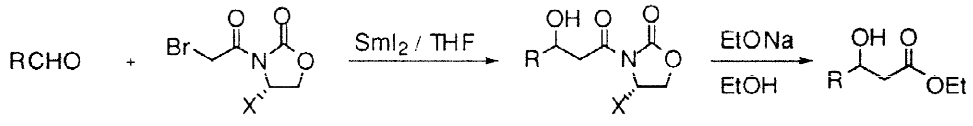
Abstract: *Samarium(II) iodide mediated highly diastereoselective Reformatsky-type reaction of chiral α-bromoacetyl-2-oxazolidinones with aldehydes.* © 1998 Elsevier Science Ltd. All rights reserved.

Samarium(II) iodide often promises highly stereoselective reactions as the result of chelation control of the samarium atom with the oxygen or nitrogen moiety in organic molecules.[1] Highly stereoselective intra- and intermolecular 1,2- and 1,3-asymmetric inductions are typical examples of this chelation control.[2] We and other research groups have recently reported a diastereoselective ketyl-alkene coupling reaction using chiral esters, acetals, and aldehydes as chiral auxiliaries.[3] We now succeeded in the highly diastereoselective intermolecular samarium-Reformatsky reaction using a chiral α-bromoacetyl-2-oxazolidinone as the chiral auxiliary.[4-6] We now present the preliminary results of this reaction.

Scheme 1



1 2: X = Pr^{i}, Ph, PhCH$_2$ 3 4

To a THF (20 ml) solution of SmI$_2$ (0.1 M, 2.0 mmol) was added a mixture of α-bromoacetyl-2-oxazolidinone (**2**) (1.0 mmol) and aldehyde (1.0 mmol) at -78 °C and the resulting mixture was stirred at the same temperature for 0.5 h during which time the color of the solution turned from deep green to yellow brown. After the usual acidic workup, the β-hydroxy carboximide (**3**) was isolated by column chromatography (SiO$_2$, hexane/ethyl acetate = 3 : 1). The diastereomeric excess (de) of **3** was determined by GC and/or HPLC. We examined the stereoselectivity of the reaction of isobutyraldehyde with three chiral oxazolidinone auxiliaries. X = Pr^{i} (78 % de), X = Ph (78 % de), and X = PhCH$_2$ (78 % de). Table 1 summarizes the results of the samarium-Reformatsky reaction of chiral α-bromoacetyl-2-oxazolidinones (**2**; X = Pr^{i}) with various aldehydes (**1**). The yields of the products were good to excellent and the de values were high for the straight chain, branched aliphatic aldehydes and aromatic aldehydes (up to 99% de). Absolute configuration of some of the products were determined by transforming into the corresponding ethyl esters.[7,8]

The origin of the high stereoselectivity has not been clarified but the reaction should proceeded *via* the samarium enolate. Further studies are now in progress.

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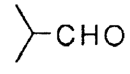
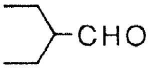
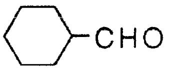
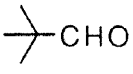
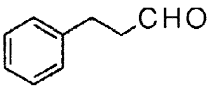
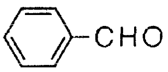
Table 1. Reaction of α-Bromoacetyl-2-oxazolidinones with Aldehydes[a]

Entry	**1**	%, yield of **3**[b]	%, de[c]	$[\alpha]_D^{25}$ of **4d**	Config.
1		92	78	+14.42 (c= 1.09, MeOH)	*R*
2		95	76		
3		78	84		
4		87	>99	+43.48 (c=1.48, $CHCl_3$)	*ND*
5	$C_7H_{15}CHO$	81	82	+10.43 (c=1.24, $CHCl_3$)	*S*
6		86	86		
7		67	64	+37.50 (c= 0.30, $CHCl_3$)	*R*

[a] **1** (1.0 mmol), **2** (1.0 mmol), SmI_2 (2.0 mmol); THF (20 ml), -78 °C, 0.5 h. [b] Isolated yield. [c] Determined by GC and/or HPLC.

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