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A New Coupling Reaction of Vinyl Esters with Aldehydes Catalyzed by Organosamarium Compounds

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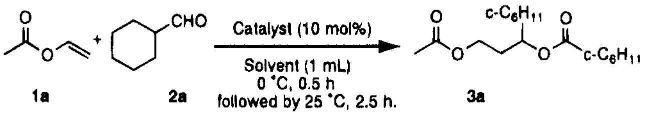
The use of organolanthanoid compounds or lanthanoid salts in organic synthesis has been steadily increasing in recent times.[1] In particular, since the time Kagan showed a convenient generation method of samarium diiodide (SmI_2), this reagent has been used in a wide variety of synthetic reactions. Although trivalent samarium species, represented by $Sm(OTf)_3$, are known to promote a variety of reactions catalyzed by Lewis acids,[2] there are only a limited number of studies on the catalytic reaction using SmI_2 (e.g., intramolecular Tishchenko reaction,[3] epoxide rearrangements,[4] Michael and Aldol reactions,[5] and Diels–Alder reactions).[6] On the other hand, samarium complexes such as $Cp^*_2Sm(thf)_2$ are reported to catalyze some reactions such as hydrogenation[7] and hydroboration of alkenes[8,9] and hydroamination/cyclization of aminoalkenes.[7a,8] More recently, Yasuda *et al.* reported that samarium complexes had a unique catalytic activity for polymerization of MMA.[10]

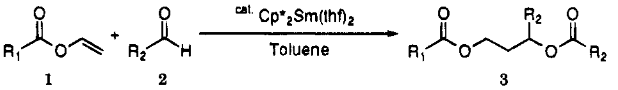
In this paper, we report on a new type of 1:2 cross coupling reaction of vinyl esters (**1**) with aldehydes (**2**) prompted by $Cp^*_2Sm(thf)_2$ and SmI_2 catalysts under mild conditions to form the corresponding diesters (**3**) in moderate to good yields (eq 1).

Table 1. Reaction of Vinyl Acetate (1a) with Cyclohexanecarboxaldehyde (2a) Catalyzed by Samarium(II) Compounds under Various Conditions



run	catalyst	ratio (**1a**/**2a**)	solvent	yield/%
1	$Cp^*_2Sm(thf)_2$	1/2	toluene	42
2	$Cp^*_2Sm(thf)_2$	1/1	toluene	77
3[a]	$Cp^*_2Sm(thf)_2$	1/1	toluene	complex mixture
4	$Cp^*_2Sm(thf)_2$	1/1	THF	59
5	SmI_2	1/1	THF	16
6	SmI_3	1/1	THF	trace
7	$Cp^*_2Sm(thf)_2$	0/1	toluene	99[b]

[a] **1a** was first added to $Cp^*_2Sm(thf)_2$ followed by **2a**. [b] Yield of 1-cyclohexylmethyl cyclohexanecarboxylate (**4**).

 (1)

A typical reaction was carried out as follows: A mixture of vinyl acetate (**1a**) (1 mmol) and cyclohexanecarboxaldehyde (**2a**) (1 mmol) was added to a catalytic amount of $Cp^*_2Sm(thf)_2$ (10 mol %) in toluene solution (1 mL) at 0 °C. The color of the $Cp^*_2Sm(thf)_2$ solution (dark purple) immediately changed to light yellow. The mixture was stirred at that temperature for 0.5 h followed by 25 °C for 2.5 h giving a 1:2 coupling product of **1a** and **2a**, 1-cyclohexanoyl-1-cyclohexyl-3-acetoxypropane (**3a**),[12] in 77% yield (run 2 in Table 1).

When **1a** was first added to the $Cp^*_2Sm(thf)_2$ solution followed by **2a**, the reaction led to a complex mixture (Table 1, run 3). The reaction in THF gave **3a** in slightly lower yield (Table 1, run 4). In this reaction, SmI_2 generated by Kagan's method[11] showed lower catalytic activity than $Cp^*_2Sm(thf)_2$ complex (Table 1, run 5), but trivalent samarium species, SmI_3, did not catalyze the present coupling reaction and the starting materials were recovered (Table 1, run 6). In contrast, the addition of **2a** to the $Cp^*_2Sm(thf)_2$ followed by **1a** led to a Tischenko product, 1-cyclohexylmethyl cyclohexanecarboxylate (**4**), rather than **3a**. In the absence of **1a**, therefore, **2a** was dimerized to **4** in almost quantitative yield (Table 1, run 7). Usually, during the stoichiometric reaction of aldehydes with divalent samarium species such as SmI_2, it is well known that pinacol coupling reactions are induced rather than Tishchenko reactions.[13]

Representative results for the $Cp^*_2Sm(thf)_2$-catalyzed coupling reactions between **1a**–**d** and aldehydes **2a**–**i** are shown in Table 2. The reaction of **1a** with aliphatic aldehydes such as acetaldehyde (**2b**), butanal (**2c**), and 2-methylpropanal (**2d**) proceeded smoothly to obtain the corresponding 1:2 coupling products in 80%, 42%, and

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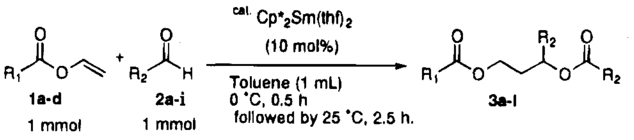
Table 2. Organosamarium-Catalyzed Coupling Reaction of Vinyl Esters with Aldehyde



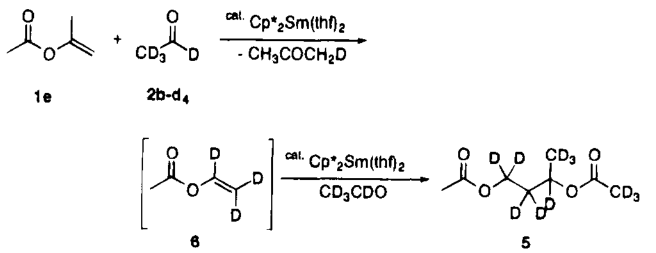
run	R_1	R_2	product[a]/%
1	CH_3 (**1a**)	c-C_6H_{11} (**2a**)	(**3a**) 77
2	**1a**	CH_3 (**2b**)	(**3b**) 80
3	**1a**	n-C_3H_7 (**2c**)	(**3c**) 42
4	**1a**	$CH(CH_3)_2$ (**2d**)	(**3d**) 70
5	**1a**	$C(CH)_3$ (**2e**)	complex mixture
6	**1a**	C_6H_5 (**2f**)	(**3f**) 77
7[b]	**1a**	(**2f**)	(**3f**) 99
8[b]	**1a**	2-$CH_3C_6H_4$ (**2g**)	(**3g**) 40
9[b]	**1a**	4-$CH_3C_6H_4$ (**2h**)	(**3h**) 59
10[b]	**1a**	4-ClC_6H_4 (**2i**)	(**3i**) 75
11	n-C_5H_{11} (**1b**)	**2f**	(**3j**) 98
12	$CH_2{=}CH$ (**1c**)	**2f**	(**3k**) 71
13	$CH_3CH{=}CH$ (**1d**)	**2f**	(**3l**) 68

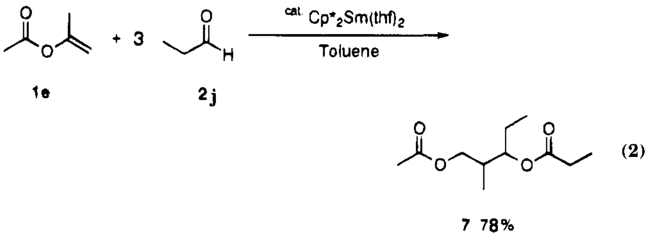
[a] GLC yields. [b] SmI_2 was used as a catalyst.

70% yields, respectively (Table 2, runs 2–4). However, trimethylacetaldehyde (**2e**) gave a complex mixture (Table 2, run 5). In the coupling reaction with aromatic aldehydes such as benzaldehyde (**2f**), SmI_2 catalyzed efficiently to give diester **3f** in almost quantitative yield (Table 2, runs 6 and 7). The same procedure for 2-methyl-, 4-methyl-, and 4-chlorobenzaldehydes (**2g**, **2h**, and **2i**) also produced the corresponding coupling products, **3g**, **3h**, and **3i**, respectively, in moderate yields (Table 2, runs 8–10).

The coupling reaction was not influenced by alkyl substituents bonded to the carbonyl group of **1**. For instance, the reaction of **2f** with vinyl hexanoate (**1b**) in the presence of $Cp^*_2Sm(thf)_2$ afforded coupling product **3j** in 98% yield (Table 2, run 11). In the reaction of **2f** with unsaturated vinyl derivatives such as vinyl crotonate (**1c**) and vinyl acrylate (**1d**), the corresponding coupling products, **3k** and **3l**, were formed in slightly lower yields (Table 2, runs 12 and 13). On the other hand, the coupling reaction of **2b** with isopropenyl acetate (**1e**) led to **3b** in 46% yield. To gain insight into the formation of **3b**, acetaldehyde-d_4 (**2b**-d_4), CD_3CDO, was employed in place of **2b**. The coupling reaction of **1e** with **2b**-d_4 afforded a 1:2 coupling product **5** in which 11 deuteriums are incorporated into the molecule. This observation suggests that the isopropenyl moiety of **1e** is easily exchanged to vinyl generated from **2b**-d_4 to form **6** on which subsequent coupling with **2b**-d_4 produces **5** (Scheme 1). In fact, the reaction of 1-butylvinyl acetate (**1f**) with **2b** afforded **3b** (57%) along with 2-hexanone (60%). In addition, the reaction of **1e** with propanal (**2j**) in the presence of $Cp^*_2Sm(thf)_2$ afforded the expected coupling product **7** in 78% yield (eq 2).

Scheme 1

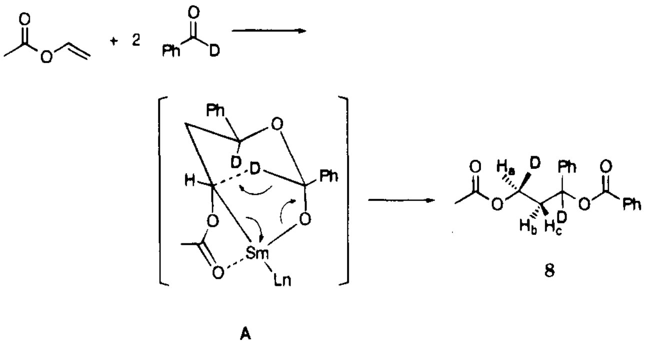




As mentioned earlier, $Cp^*_2Sm(thf)_2$ catalyzes the Tishchenko reaction of cyclohexanecarboxaldehyde **2a** to give ester **4** in quantitative yield (run 5 in Table 1). Therefore, 1:2 coupling product may be formed *via* successive reaction between ester, the dimerization product of aldehyde, and vinyl acetate. Thus, the reaction of **1a** with benzyl benzoate, obtained by Tishchenko reaction of benzaldehyde **2f**, was carried out in the presence of $Cp^*_2Sm(thf)_2$, but **3f** was not formed. Consequently, the reaction path by way of ester as the transist intermediate is excluded for the formation of **3f**. In order to obtain mechanistic information concerning the present reaction, the coupling of **1a** was studied using benzaldehyde-*formyl-d* (PhCDO). As expected, the reaction gave 1:2 adduct, **8**, in which two deuterium were incorporated into the alkoxy moiety of **8**.[14]

On the basis of the labeling study, Scheme 2 is proposed as a plausible reaction path for this coupling reaction. The mechanism might involve an eight-membered alkoxy samarium species (**A**) which is the key intermediate in the present reaction. A subsequent intramolecular hydride shift reaction produces the diester,[14] and the samarium species is regenerated. The proposed transition state closely resembles the Sm-catalyzed intramolecular Tischenko reaction of α-hydroxy ketones and Reformatsky reaction of Evans[3] and Molander,[13a] respectively.

Scheme 2. A Plausible Reaction Path



Further studies along this line and the investigation of the detailed reaction mechanism are now in progress.

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Supporting Information Available: Procedures and characterization data (8 pages).

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(14) The ^1H NMR of H_a proton in the coupling product **8** exhibited a triplet ($J_{ab} \approx J_{ac} = 6.1$ Hz) at δ 4.10 indicating that the **8** consists of a single component between two possible diastereoisomers.[14] This fact may suggest that the coupling reaction proceeds via intramolecular hydride shift from a cyclic intermediate (**A**).