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Facile Isomerization of Trimethylsilyl Ketene Acetals to α-Trimethylsilyl Esters Catalyzed by Lanthanoid Trifluoromethanesulfonates

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Migration of trimethylsilyl group from oxygen to α-carbon in silyl ketene acetals is effectively catalyzed by lanthanoid triflates under mild conditions. Scope and limitation of this rearrangement are presented.

Thermal migration of trialkylsilyl group from carbon to oxygen in α-silyl ketones has been well established.1) The reverse process has been also observed in silyl ketene acetals,2) but less common because of competitive decomposition to ketenes and trialkylsilyl ethers.3) In addition, Lewis acid catalyzed migration of the silyl group from O to α-C has been rarely documented: one is the reaction with HgI_2 4) and the other is that with $[Cp_2Zr(O^tBu)THF][BPh_4]$,5) in which Mukaiyama aldol reaction can be performed using the two Lewis acids in the presence of aldehydes.6) In contrast, silyl ketene acetals are oxidatively dimerized into succinates by the treatment with $TiCl_4$.7)

Recently, we have reported aldol reaction of silyl ketene acetals with aldehydes promoted by lanthanoid (II) and (III) alkoxides,8) wherein the reaction with a divalent alkoxide shows better diastereoselectivity than that with a trivalent alkoxide even if semicatalytic amounts of the alkoxides are used. To test the possibility of reduction of the lanthanoid (III) with silyl ketene acetals, we have treated the acetals with various lanthanoid Lewis acids and found that a facile migration of the silyl group from O to α-C takes place without the redox reaction. We report herein the scope and limitation of this reaction.

When a solution of (E)-1-ethoxy-1-trimethylsilyloxy-1-propene (**1c**) in dichloromethane (0.4 M) was treated with ytterbium(III) trifluoromethanesulfonate (1 mol%) at room temperature for 2 h, ethyl 2-trimethylsilylpropionate (**2c**) was formed in quantitative yield.9) Results using various lanthanoid Lewis acids are summarized in Table 1. Samarium and lanthanum triflates catalyzed the isomerization in high yields, although their activities were a little lower than that of $Yb(OTf)_3$ (Runs 1-3). In the reaction with $YbCl_3$ and $SmCl_3$, the acetal **1c** remained unchanged (Runs 4 and 5). Longer reaction time caused the slow decomposition of **1c** to ethyl propionate (32% yield after 48 h in Run 4), but **2c** was not formed. Similarly, $Yb(fod)_3$ and $Yb(tfc)_3$ did not promote the isomerzation (Runs 6 and 7).10) With respect to Lewis acids other than lanthanoids, $BF_3{\cdot}OEt_2$ (10 mol%) was of no effect under the reaction conditions. ZnI_2 (1 mol%) catalyzed the rearrangement quantitatively within 2 h, showing same catalyst activity as $Yb(OTf)_3$ in dichloromethane. However the reaction with ZnI_2 did not take place in THF, whereas $Yb(OTf)_3$ was also active in this solvent, *vide infra.*

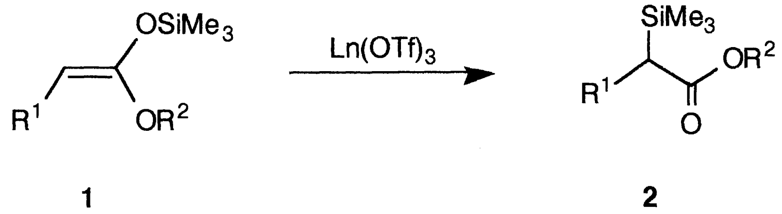

Table 1. Isomerization of (E)-1-Ethoxy-1-trimethylsilyloxy-1-propene (**1c**) to Ethyl 2-Trimethylsilylpropionate (**2c**) Catalyzed by Lanthanoid Lewis Acids[a)]

Run	Lewis Acid	Mol%	Time/h	Yield/%[b)]
1	$Yb(OTf)_3$	1	2	>99
2	$Sm(OTf)_3$	1	7	>99
3	$La(OTf)_3$	1	7	87
4	$YbCl_3$	10	7	0
5	$SmCl_3$	10	7	0
6	$Yb(fod)_3$[c)]	10	7	0
7	$Yb(tfc)_3$[d)]	10	7	0

a) Conditions : CH_2Cl_2 (0.4 M), rt. b) GC yield. c) Tris(6, 6, 7, 7, 8, 8, 8-heptafluoro-2, 2-dimethyl-3, 5-octanedionato) ytterbium(III).
d) Tris[3-(trifluoromethylhydroxymethylene)camphorato] ytterbium(III).

Table 2. Effect of Solvent and Amount of $Yb(OTf)_3$ on the Isomerization of **1c** to **2c**[a)]

Run	Solvent	Amount of $Yb(OTf)_3$/mol%	Time/h	Yield/%[b)]
1	CH_2Cl_2	2.5	2	>99
2	CH_2Cl_2	1.0	2	>99
3	CH_2Cl_2	0.5	2	>99
4	CH_2Cl_2	0.25	2	94
5	CH_2Cl_2	0.1	2	57
6	CH_2Cl_2	0.1	7	87
7	$ClCH_2CH_2Cl$	1.0	2	>99
8	CH_3CN	1.0	2	85
9	THF	1.0	7	89
10	Toluene	1.0	7	38
11	n-Hexane	1.0	7	0

a) Conditions: 0.4 M solution, rt. b) GC yield.

Table 3. Isomerzation of Trimethylsilyl Ketene Acetals **1** to α-Trimethylsilyl Esters **2**[a)]

Run	Substrate	R^1	R^2	Time/h	Product	Yield/%[b)]
1	**1a**	H	Et	5min	**2a**	94
2	**1b**	Me	Me	2	**2b**	95
3	**1c**	Me	Et	2	**2c**	>99
4	**1d**	Me	^{i}Pr	2	**2d**	>99
5	**1e**	Et	Me	7	**2e**	>99
6	**1f**[c)]	$PhCH_2$	Me	10	**2f**	90

a) Conditions: $Yb(OTf)_3$ 1 mol%, CH_2Cl_2 (0.4 M), rt. b) GC yield.
c) A mixture of E and Z isomers (2 : 1).

Since $Yb(OTf)_3$ exhibited the highest catalyst activity among the Lewis acids tested, the effect of solvent and amount of the triflate on the reaction of the acetal **1c** was investigated (Table 2). In dichloromethane, the yield of **2c** decreased as the amount of $Yb(OTf)_3$ decreased (Runs 3-5), but the yield increased with increasing of the reaction time in the case of 0.1 mol% of the catalyst (Runs 5 and 6). Dichloromethane and dichloroethane were suitable solvents for the isomerization (Runs 2 and 7). In acetonitrile and THF, the reaction took place in lower yields (Runs 8 and 9). On the other hand, little or no isomerization was observed in toluene and hexane, which was ascribed in part to insolubility of $Yb(OTf)_3$ in these solvents (Runs 10 and 11).

Next various trimethylsilyl ketene acetals were isomerized using $Yb(OTf)_3$ catalyst in dichloromethane (Table 3). All substrates shown in Table 3 were converted into α-trimethylsilyl esters in high yields. However longer reaction time was needed for the isomerization as the substituent at α-carbon (R^1) became larger, while ester moiety (R^2) was likely to have less influence on the reaction (Runs 2-4). In contrast, trimethylsilyl ketene acetals derived from ethyl isobutyrate, methyl phenylacetate, and methyl 3-phenylbutyrate were decomposed to the corresponding esters quantitatively and no α-silylated products were obtained. Furthermore, (E)-1-dimethylethylsilyloxy-1-ethoxy-1-propene (**3**) isomerized to ethyl 2-dimethylethylsilylpropionate (**4**) in 95% yield under similar conditions (7 h), whereas 1-*tert*-butyldimethylsilyloxy-1-ethoxyethene was recovered unchanged.

Then the reaction of trimethylsilyl ketene acetal **1b** was monitored by ^{13}C NMR in dichloromethane using $La(OTf)_3$ (10 mol%). Signals of the trimethylsilyl group of **1b** and the product **2b** appeared at -0.65 and -3.35 ppm, respectively and an additional new signal was observed at -0.15 ppm, which was assigned to that of trimethylsilyl triflate by comparison of the spectra of an authentic sample. Intensity ratio of the three silyl groups was 87 : 7 : 6 at 15 min and 37 : 57 : 6 at 3.5 h.[11)] These results suggest that the migration of the silyl group proceeds via initial generation of lanthanum enolate[12)] and TMSOTf, followed by C-silylation of the enolate.[13)] Therefore the migration catalyzed by lanthanoid triflates should be an intermolecular process. In fact, when a mixture of equimolar amounts of **1d** and **3** was treated with $Yb(OTf)_3$, crossover products, isopropyl 2-dimethylethylsilylpropionate and ethyl 2-trimethylsilylpropionate were obtained in 35% and 28% yields, respectively along with **2d** (57%) and **4** (33%).

In summary, lanthanoid triflates have been found to act as unique Lewis acids to catalyze the migration of trimethylsilyl group from O to α-C in silyl ketene acetals in high yields under mild conditions, which offers a convenient method for the preparation of α-silyl esters$^{14)}$ in connection with their advantage of low toxicity, easy handling, and reusability.$^{15)}$

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