An Efficient Acylation of Tertiary Alcohols with Isopropenyl Acetate Mediated by an Oxime Ester and $Cp^*_2Sm(thf)_2$

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An efficient method for the acylation of tertiary alcohols with isopropenyl acetate (**1**) by the use of an oxime and $Cp^*_2Sm(thf)_2$ as catalyst was developed. Thus, various types of tertiary alcohols could be acylated with **1** in the presence of a catalytic amount of cyclohexanone oxime acetate (**2**) and $Cp^*_2Sm(thf)_2$ under mild conditions to form the corresponding acetates in excellent yields. Acid-sensitive terpene alcohols such as linalool were successfully acetylated by the present method to give acetyl linalool in quantitative yield. This method enables an alternative acylation of tertiary alcohols under acid-free conditions.

1. Introduction

The acetylation of the hydroxy function of alcohols is an important and frequently used transformation in organic synthesis.[1] Acetic anhydride[2] and acetyl chloride[3] are usually used as the acylating agents. To increase the rate of acylation, the reaction is carried out in the presence of a protic or Lewis acid catalyst.[4] It is well-known that the acylation of alcohols with acid anhydride is facilitated by tributylphosphine[5] or pyridine derivatives such as 4-(dimethylamino)pyridine and 4-pyrrolidine.[6] More recently, $Sc(OTf)_3$[7,8] and TMSOTf[9] have been reported to be efficient catalysts for the acetylation of alcohols with acetic anhydride or acetic acid under mild conditions. However, the acylation using acetic anhydride as the acylating agent is accompanied by the concomitant formation of acetic acid in the course of the reaction. As a consequence, these methods are unfavorable for the acylation of acid- and base-sensitive compounds. Hence, it is important to develop an efficient acylating method under acid or base free conditions.

Since oxime esters are reported to be good acylating agents of amines to the corresponding amides,[10] they are powerful candidates for elucidating the acylation under neutral conditions. Even if oximes are generated during the acylation of alcohols with the oxime esters, they are extremely weak acids (pK_a *ca.* 11) compared with acetic acid (pK_a 5.1).

In a previous paper, we showed that $Cp^*_2Sm(thf)_2$ catalyzes the acylation of alcohols and amines with vinyl- and isopropenyl acetates under ambient conditions.[11] However, the drawback to this method is that tertiary alcohols are difficult to be acylated in satisfactory yields.

Now, we have found a novel double-mediated acylating method, using an oxime ester and $Cp^*_2Sm(thf)_2$, for tertiary alcohols with isopropenyl acetate (**1**). Thus, the acylation of a variety of tertiary alcohols with **1** could be achieved by the use of cyclohexanone oxime acetate (**2**) and $Cp^*_2Sm(thf)_2$ under mild and acid-free conditions.

2. Results and Discussion

Tertiary alcohol, 2-methyl-2-hexanol (**3**), was chosen as a model substrate and allowed to react with **1** in the presence of **2** and $Cp^*_2Sm(thf)_2$ under various reaction conditions (eq 1, Table 1).

Tertiary alcohol **3** was successfully acetylated with 2 equiv of **1** and a stoichiometric amount of **2** by $Cp^*_2Sm(thf)_2$ (10 mol %) at room temperature to give 2-methyl-2-hexyl acetate (**4**) in quantitative yield (run 1). However, results of the same reaction of **3** in the absence of either **1** or **2** under these conditions were unsatisfactory (runs 2 and 3). The acylation of tertiary alcohol **3** using vinyl acetate (**5**) in place of **1** under these conditions led to a low yield of **4** (run 4). It is interesting to note that **3** was acetylated with **1** by the use of a catalytic amount of oxime ester **2** (20 mol %) to form **4** in excellent yield (run 5). Even when the amount of the $Cp^*_2Sm(thf)_2$ employed was halved, **4** was obtained in high yield (90%) (run 6). Needless to say, in the absence of the catalyst, no **4** was formed (run 8). Lanthanide

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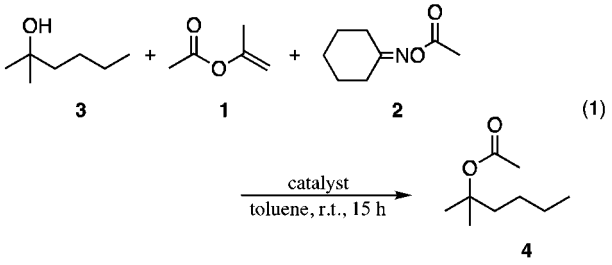
Table 1. $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of 2-Methyl-2-hexanol (3) with Isopropenyl Acetate (1) in the Presence of Cyclohexanoneoxime Acetate (2)[a]

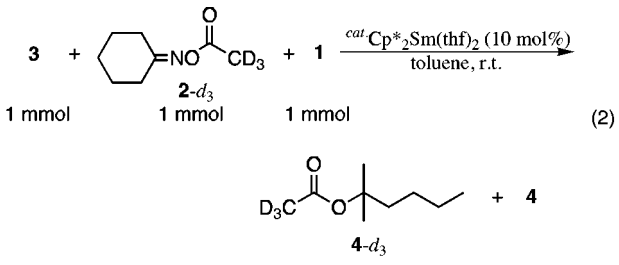


run	catalyst (mmol)	**1**/mmol	**2**/mmol	**4**/%
1	$Cp^*_2Sm(thf)_2$ (0.1)	2	1	>99
2	$Cp^*_2Sm(thf)_2$ (0.1)	0	2	18
3	$Cp^*_2Sm(thf)_2$ (0.1)	2	0	34
4[b]	$Cp^*_2Sm(thf)_2$ (0.1)	2	1	15
5	$Cp^*_2Sm(thf)_2$ (0.1)	2	0.2	>99
6	$Cp^*_2Sm(thf)_2$ (0.05)	2	0.2	90
7	$Cp^*_2Sm(thf)_2$ (0.01)	2	0.2	81
8	No catalyst	2	1	No reaction
9	$Cp^*_2Yb(thf)_2$ (0.1)	2	1	70
10	$Sm(O^iPr)_3$ (0.1)	2	1	51
11	$Sm(OTf)_3$ (0.1)	2	1	2
12[c]	SmI_2 (0.1)	2	1	10

[a] **3** (1 mmol) was allowed to react with **1** in the presence of **2** and $Cp^*_2Sm(thf)_2$ (0.1 mmol) in toluene (1 mL) for 15 h. [b] Vinyl acetate (**5**) was used in place of **1**. [c] THF (1 mL) was used as a solvent.

compounds other than $Cp^*_2Sm(thf)_2$ were examined. $Cp^*_2Yb(thf)_2$ was also efficient for the present reaction, although the yield of **4** decreased slightly than that by $Cp^*_2Sm(thf)_2$ (run 9). The same reaction using $Sm(O^iPr)_3$ as the catalyst produced **4** in moderate yield (51%) (run 10), but the reaction by $Sm(OTf)_3$ and SmI_2 took place with some difficulty to give **4** in low yields (runs 11 and 12).

To gain information on the reaction path for the acylation of **3**, a 1:1 mixture of **1** and cyclohexanone oxime acetate-d_3 (**2**-d_3) was allowed to react with **3** in the presence of $Cp^*_2Sm(thf)_2$ (eq 2). Time-dependence curves for the acylation of **3** show that the **3** reacts more easily with **2**-d_3 than with **1** to form deutrated acetate, **4**-d_3, in preference to **4** (Figure 1). This result indicates that the oxime ester **2** is more reactive than the isopropenyl acetate **1**.



The acylation of alcohols by the present system, therefore, is illustrated as Scheme 1. It is thought that the alcohol **3** reacts with oxime ester **2** in the presence of $Cp^*_2Sm(thf)_2$ to produce the ester **4** and cyclohexanone oxime (**6**) which subsequently reacts with **1** to generate **2**. The fact that the present acylation was only achieved by the coexistence of both **1** and **2** indicates that the oxime **6** derived from **2** smoothly reacted with **1** in the presence of $Cp^*_2Sm(thf)_2$ to rapidly regenerate **2**. Indeed, **6** was found to react very fast with **1** under the influence

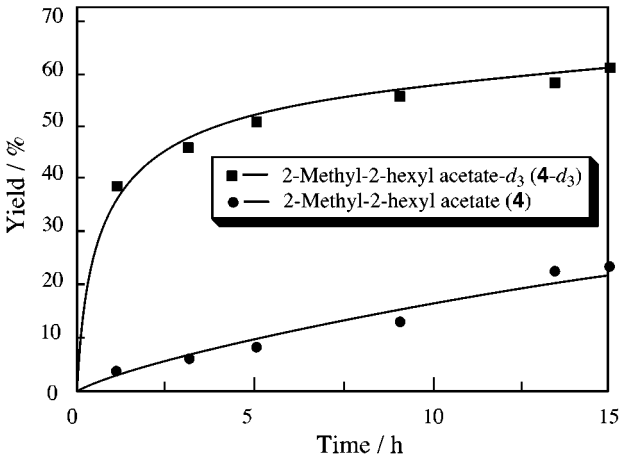
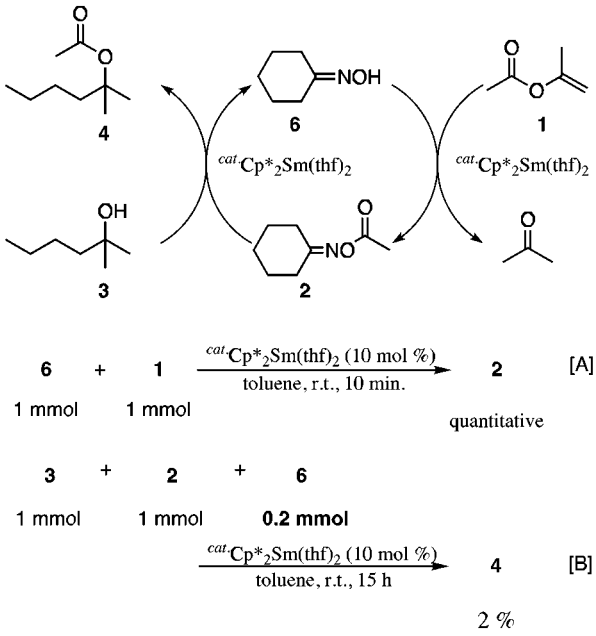


Figure 1. $Cp^*_2Sm(thf)_2$-catalyzed acylation of 2-methyl-2-hexanol (**3**) with cyclohexanone oxime acetate-d_3 (**2**-d_3) and isopropenyl acetate (**1**).

Scheme 1. Possible Reaction Path of $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of Alcohol 3 using Oxime Acetate 2 and Isopropenyl Acetate (1)



of $Cp^*_2Sm(thf)_2$ at room temperature, forming **2** in quantitative yield (Scheme 1A). Although the oxime ester **2** serves as a favorable acylating agent of alcohols, the resulting oxime **6** was found to retard the acylation. The reaction of alcohol **3** with **2** in the presence of a small amount of **6** under these conditions led to **4** in poor yield (2%) (Scheme 1B).

A real active species in this reaction seems to be a samarium alkoxy compound derived from $Cp^*_2Sm(thf)_2$ and alcohol used, since $Cp^*_2Sm(thf)_2$ reacts readily with protic compounds such as alcohols to produce the corresponding alkoxides.[12]

In fact, the independent reaction of $Cp^*_2Sm(thf)_2$ with 2-propanol in the presence of acrylonitrile at room temperature for 3 h produced Diels–Alder adduct, 5-cyano-1,2,3,4,7-pentamethyl-2-norbornene (**7**), in 81% yield

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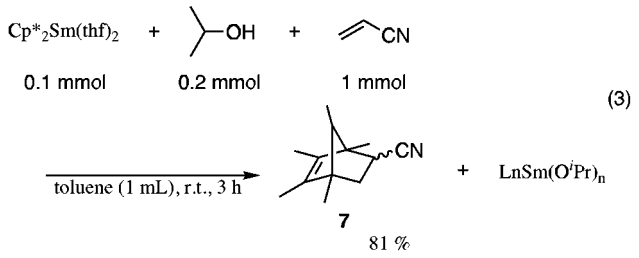
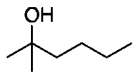
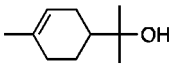
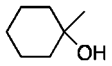
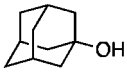
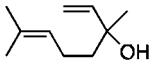
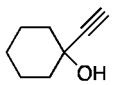
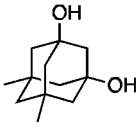
along with an alkoxy samarium species, $LnSm(OiPr)_n$,[13] whose structure is not identified at the present time (eq 3).



(3)

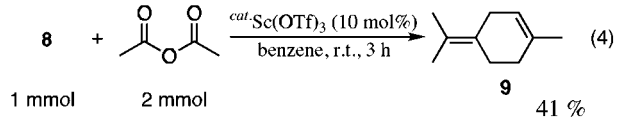
On the basis of these results, the acylation of various tertiary alcohols with **1** was examined under the influence of a catalytic amount of oxime ester **2** and $Cp^*_2Sm(thf)_2$ (Table 2).

Table 2. $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of Various Tertiary Alcohols with Cyclohexanone Oxime Acetate (2) and Isopropenyl Acetate (1)[a]

run	3° alcohol	temp. / °C	acetate (yield / %)
1	 (**3**)	25	>99
2		50	90
3		25	92
4		50	98
5	 (**8**)	50	>99
6		50	90
7		25	>99
8		50	>99[b]

[a] Alcohol (1 mmol) was allowed to react with **1** (2 mmol) in the presence of **2** (0.2 mmol) and $Cp^*_2Sm(thf)_2$ (0.1 mmol) in toluene (1.0 mL) for 15 h. [b] Yield of 5,7-dimethyl-1.3-adamantandiol diacetate.

As mentioned above, **3** reacted with **1** in the presence of catalytic amounts of **2** and $Cp^*_2Sm(thf)_2$ at room temperature to give acetate **4** in almost quantitative yield (run 1). α-Terpineol was acetylated at somewhat higher temperature (50 °C) to afford α-terpinyl acetate in 90% yield (run 2). Cyclic tertiary alcohols, 1-methyl-1-cyclohexanol and 1-adamantanol, were respectively acetylated at 25 °C and 50 °C, giving 1-methyl-1-cyclohexyl acetate and 1-adamantyl acetate in high yields (runs 3 and 4). It is of interest to note that the reaction of acid-sensitive alcohols such as linalool (**8**) took place without the allylic rearrangement or the dehydration to form linalyl acetate in almost quantitative yield (run 5), although the same acylation of **8** using acetic anhydride and $Sc(OTf)_3$ resulted in a dehydration product, terpinolene (**9**), rather than the acetate (eq 4). Other acid-sensitive substrates

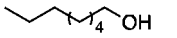
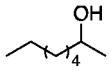
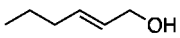
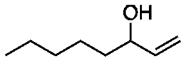


(4)

such as 1-ethynyl-1-cyclohexanol and 2-phenyl-2-propanol gave the corresponding acetates in excellent yields (runs 6 and 7). 5,7-Dimethyl-1,3-adamantanediol, prepared by the oxidation of 1,3-dimethyladamantane with O_2 (1 atm) with the aid of a radical catalyst, *N*-hydroxyphthalimide (NHPI),[15] gave quantitatively diacetate with a trace amount of monoacetate (run 8). The successful acylation of all the tertiary alcohols used by **1** in the presence of catalytic amounts of **2** and $Cp^*_2Sm(thf)_2$ under acid-free conditions, which we have achieved, is indeed a promising methodology.

On the other hand, secondary and primary alcohols were efficiently acetylated with **2** even in the absence of **1** (Table 3).

Table 3. $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of Primary and Secondary Alcohols with Cyclohexanone Oxime Acetate (2)[a]

run	alcohol	time / h	acetate / %
1		<0.1	>99
2		8 (<0.1)[b]	87 (>99)[b]
3		<0.1	>99
4		8(<0.1)[b]	76 (>99)[b]

[a] Alcohol was allowed to react with **2** (2 mmol) in toluene (1 mL) in the presence of $Cp^*_2Sm(thf)_2$ (0.1 mmol) at room temperature. [b] A number of parenthesis represents the yield when **1** (2 mmol) was added to the reaction system.

1-Octanol was easily acylated with 2 equiv of **2** within 0.1 h under ambient conditions to give octyl acetate in quantitative yield (run 1). A secondary alcohol such as 2-octanol was slowly acetylated with **2** under these conditions (run 2). However, when **1** was added to the above reaction system, 2-octyl acetate was readily formed in quantitative yield. Allylic alcohols such as *trans*-2-hexen-1-ol and 1-octen-3-ol were acetylated without any side reaction such as the isomerization or the allylic rearrangement to give the corresponding acetates in quantitative yields (runs 3 and 4).

(13) ^1H NMR measurement of the reactant obtained from the reaction of $Cp^*_2Sm(thf)_2$ and 2-propanol showed signals assigned to 1,2,3,4,5-pentamethylcyclopentadiene (δ 0.99 (d, 3H, J = 7.8 Hz), 1.73 (s, 6H), 1.79 (s, 6H), 2.36−2.52 (m, 1H)) and broad signals characteristic to a low valent samarium species (δ 1.35−1.51, 3.50−3.67) in contrast to that of $Sm(OiPr)_3$.[14] This observation may be suggest the generation of a samarium species such as $LnSm(OiPr)_2$.

(14) (a) Turova, N. Y.; Kozunov, V. A. J. *Inorg. Nucl. Chem.* **1979**, *41*, 5. (b) Akitt, J. W.; Duncan, R. H. *J. Magn. Reson.* **1874**, *15*, 162.
(15) Ishii, Y.; Kato, S.; Iwahama, T.; Salaguchi, S. *Tetrahedron Lett.* **1996**, *37*, 4993.

In conclusion, an efficient acylating method for various alcohols, especially tertiary alcohols, was achieved by using isopropenyl acetate **1** with the aid of oxime ester **2** and $Cp^*_2Sm(thf)_2$ under neutral conditions. This method provides a novel approach for the acylation of tertiary alcohols under acid-free conditions.

Experimental Section

General Procedure. ^1H and ^{13}C NMR measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. IR spectra were measured as thin films on NaCl plate or KBr press disk. GLC analysis was performed with flame ionization detector using 1 mm × 30 m capillary column (OV-1). Mass spectra were determined at an ionizing voltage of 70 eV. Vinyl esters and alcohols were purchased from a commercial origin and distilled prior to use. $Cp^*_2Sm(thf)_2$,[16] $Cp^*_2Yb(thf)_2$,[16] $Sm(OiPr)_3$,[17] $Sm(OTf)_3$,[18] and SmI_2[19] were prepared according to literature procedures. Cyclohexanone oxime acetate (**2**) was prepared by cyclohexanone oxime and acetic anhydride according to literature procedure.[20] Cyclohexanoneoxime acetate-d_3 (**2**-d_3) was prepared by cyclohexanoneoxime and acetyl chloride-d_3.

General Procedure for the $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of Alcohols with Oxime Acetate and Isopropenyl Acetate. To a Schlenk tube containing toluene solution (1 mL) of $Cp^*_2Sm(thf)_2$ (0.1 mmol) were slowly added alcohols (1 mmol) followed by cyclohexanone oxime acetate (**2**) (0.2−2.0 mmol) and isopropenyl acetate (2 mmol) (**1**) under argon. When the reaction was complete, wet diisopropyl ether (10 mL) was added to the solution, and the catalyst was removed by filtration. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (20/1 v/v) as eluent to give the corresponding acetates. The acetates were identified through comparison of the isolated acetates with authentic samples.

Reaction of $Cp^*_2Sm(thf)_2$ with 2-Propanol in the Presence of Acrylonitrile. To a Schlenk tube containing toluene solution (1 mL) of $Cp^*_2Sm(thf)_2$ (0.1 mmol) was slowly added 2-propanol (0.2 mmol) and stirred at room temperature for 10 min under argon. Subsequently, to the solution was added acrylonitrile (1 mmol) and stirred at room temperature for 3 h. The reaction mixture was quenched with wet diisopropyl ether (10 mL), and the catalyst was removed by filtration. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (20/1 v/v) as eluent to give a stereoisomeric mixture of 5-cyano-1,2,3,4,7-pentamethyl-2-norbornene (**7**) in 81% yield.

$Sc(OTf)_3$-Catalyzed Reaction of Linalool. To a solution linalool (**8**) (1 mmol) in benzene (1 mL) was added $Sc(OTf)_3$ (0.1 mmol) and stirred at room temperature for 3 h. The solution was quenched with water, and the product was extracted with $CHCl_3$. The organic layers were dried over magnesium sulfate. After removal of magnesium sulfate by filtration, the solvent was evaporated under reduced pressure to afford a yellow liquid. Purification of the product by column chromatography on silica gel with *n*-hexane/ethyl acetate (10/1 v/v) as eluent gave the terpinolene (**9**) in 41% yield.

Cyclohexanoneoxime acetate-d_3 (2-d_3): ^1H NMR ($CDCl_3$/TMS) δ 1.58−1.85 (m, 6H), 2.38 (m, 2H), 2.55 (m, 2H). ^{13}C NMR ($CDCl_3$/TMS) δ 18.5, 18.8, 19.1, 25.2, 25.6, 26.6, 26.7, 31.7, 31.9, 168.4, 168.8. IR (neat) 876, 1061, 1205, 1234, 1450, 1641, 1759, 1937 cm^{-1}.

5-Cyano-1,2,3,4,7-pentamethyl-2-norbornene: ^1H NMR ($CDCl_3$/TMS) δ 0.55−0.64 (m, 3H), 1.02−1.09 (m, 3H), 1.16−1.26 (m, 3H), 1.27−1.93 (m, 9H), 2.10 (q, J = 4.6 Hz, 0.4H), 2.58 (q, J = 4.6 Hz, 0.6H). ^{13}C NMR ($CDCl_3$/TMS) δ 7.9, 8.0, 9.3, 9.5, 9.6, 9.6, 9.8, 11.1, 11.3, 13.1, 13.4, 14.1, 14.7, 34.9, 35.1, 36.9, 38.1, 40.9, 14.7, 53.3, 53.4, 57.4, 57.6, 58.0, 59.5, 60.2, 61.1, 122.6, 122.9, 132.1, 132.3, 136.6, 137.0. IR (neat) 1023, 1080, 1380, 1454, 2234, 2873, 2959 cm^{-1}. MS (70 eV) m/e = M^+ 189 (9), 149 (5), 136 (99), 121 (100).

5,7-Dimethyl-1,3-adamantanediol diacetate: ^1H NMR ($CDCl_3$/TMS) δ 0.88 (m, 6H), 1.08 (m, 2H), 1.70 (m, 8H), 1.89 (s, 6H), 2.28 (m, 2H). ^{13}C NMR ($CDCl_3$/TMS) δ 22.4, 28.9, 34.6, 43.6, 46.0, 49.3, 81.2, 170.1. IR (neat) 973, 1025, 1182, 1229, 1367, 1462, 1732, 2866, 2951 cm^{-1}.

Terpinolene: ^1H NMR ($CDCl_3$/TMS) δ 1.61−1.78 (m, 9H), 1.93−2.03 (m, 2H), 2.32 (t, J = 6.2 Hz, 2H), 2.73 (m, 2H), 5.34−5.41 (m, 1H). ^{13}C NMR ($CDCl_3$/TMS) δ 19.7, 20.2, 23.4, 26.6, 29.5, 31.4, 120.8, 121.7, 127.6, 134.2. IR (neat) 1374, 1446, 2909, 2965 cm^{-1}.

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