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# Acetalization of Ketones and Aldehydes Catalyzed by Lanthanoid Trisulfonates

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**Lanthanoid sulfonates are found to be good catalysts for the acetalization of aldehydes and ketones with methyl orthoformate in methanol. The catalytic activity of $Ln(OTf)_3$ (OTf, trifluoromethanesulfonate) increases in the order of La < Sm < Gd < Er < Yb. As sulfonates such as trifluoromethylsulfonates and (1*S*)-10-camphorsulfonates are more soluble in organic solvents than the chlorides, the acetalization in ether or dichloromethane and the exchange reaction of alkoxy groups between acetals and alcohols can be achieved under mild conditions.**

**Keywords: acetalization; lanthanoid trisulfonate; orthoformate; ester exchange reaction**

## INTRODUCTION

Acetalization is among the most frequently used reactions for the protection of carbonyl groups in organic synthesis. Since mineral acids are commonly used as the catalysts, acetalization is occasionally accompanied by serious side reactions. Recently, lanthanoid trichlorides have been reported to be the best catalysts[1] to have been widely used.[2] The acetalization of aldehydes is achieved with minimal side reactions[1,3] and with high chemoselectivity.[4] However, lanthanoid trichlorides are not effective for the acetalization of ketones.[1b,4] Another disadvantage is the insolubility of lanthanoid trichlorides in organic solvents except methanol and ethanol. Therefore, we investigated the applicability of lanthanoid sulfonates as catalysts for acetalization.

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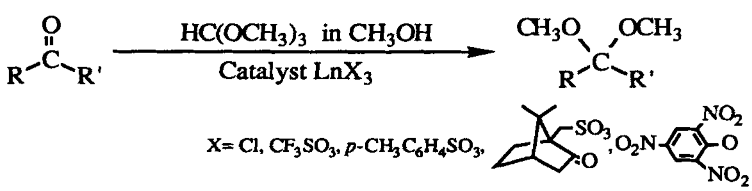
## RESULTS AND DISCUSSION

In this study, lanthanoid trifluoromethanesulfonates [$Ln(OTf)_3$], *p*-toluenesulfonate [$Ln(OTs)_3$], (1*S*)-10-camphorsufonates [$Ln(OCas)_3$], and 2,4,6-trinitrophenoxide [$Ln(Pic)_3$] were tested. These ytterbium complexes are very soluble in methanol, but insoluble in anhydrous ether, dichloromethane and THF. Interestingly, these compounds are soluble in those solvents when they contained small amounts of DMF, methanol or water (0.5–3 vol%) at room temperature. However, $YbCl_3 \cdot 6H_2O$ could not be solubilized by the addition of such amounts of the cosolvents.

The catalytic activity of these ytterbium complexes was compared in the acetalizations of bezaldehyde and acetophenone with methyl orthoformate in methanol (Eqn [1]). The results are summarized in Table 1. The reaction of benzaldehyde in the presence of any of the catalysts including $YbCl_3 \cdot 6H_2O$ readily proceeded at 20 °C and gave an almost quantitative yield of benzaldehyde dimethyl acetal. The acetalization of acetophenone was carried out at 40 °C for 3 h. The catalytic activity of lanthanoid chlorides was not great enough under these conditions, as known previously.[1b] Ytterbium trifluoromethanesulfonate was very reactive, and a quantitative yield of acetophenone dimethyl acetal was obtained without by-products. The catalytic activity of the other sulfonates was approximately




[1]

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**Table 1** Catalytic activity of lanthanoid(III) compounds in the acetalization of benzaldehyde and acetophenone with methyl orthoformate in methanol

| | Yields of acetals[a] (%) | |
|---|---|---|
| Catalyst | $PhCHO^{b}$ | $PhCOCH_3{}^{c}$ |
| $YbCl_3 \cdot 6H_2O$ | 98 | 18 |
| $LaCl_3 \cdot 6H_2O$ | — | 6 |
| $Yb(OTf)_3{}^{d}$ | 99 | 98 |
| $Yb(OTs)_3 \cdot 9H_2O^{e}$ | 98 | 29 |
| $Yb(OCas)_3 \cdot \frac{1}{2}THF^{f}$ | 98 | 12 |
| $La(OCas)_3 \cdot \frac{1}{2}THF^{f}$ | — | 10 |
| $Yb(Pic)_3 \cdot 7H_2O^{g}$ | 84 | 5 |

[a] The reaction was carried out by stirring a mixture of catalyst and carbonyl compound in methanol (5 $cm^3$) and the yield was determined by GLC using internal standards.
[b] Reaction conditions: PhCHO (5 mmol), $HC(OCH_3)_3$ (10 mmol), catalyst (0.025 mmol), at 20 °C for 30 min.
[c] Reaction conditions: $PhCOCH_3$ (5 mmol), $HC(OCH_3)_3$ (10 mmol), catalyst (0.05 mmol), at 40 °C for 4 h.
[d] $Tf = CF_3SO_2$.
[e] $Ts = p\text{-}CH_3C_6H_4SO_2$.
[f] Cas = (1*S*)-10-camphorsulfonyl.
[g] Pic = 2,4,6-trinitrophenoxyl.

equal to the lanthanoid chlorides. $Yb(Pic)_3 \cdot 7H_2O$ was less reactive than the chlorides. Interestingly, the catalytic activities of ytterbium compounds were higher than those of the corresponding lanthanum compounds.

The chemoselectivity was examined in the acetalization of an equimolar mixture of benzaldehyde and cyclohexanone (see Table 2). The aldehyde acetalized faster than the ketone in all reactions. In the reactions with the sulfonate catalysts, the ratios of benzaldehyde dimethyl

**Table 2** Chemoselectivity of ytterbium(III) compounds in the acetalization of a mixture of benzaldehyde and cyclohexanone

| | Yields[a] (%) | | |
|---|---|---|---|
| Catalyst | $PhCH(OCH_3)_2$ | $C_6H_{10}(OCH_3)_2$ | Ratio[b] |
| $YbCl_3 \cdot 6H_2O$ | 86 | 15 | 5.7 |
| $Yb(OTf)_3$ | 88 | 18 | 4.9 |
| $Yb(OTs)_3 \cdot 9H_2O$ | 84 | 15 | 5.3 |
| $Yb(OCas)_3 \cdot \frac{1}{2}THF$ | 77 | 14 | 5.5 |
| $Yb(Pic)_3 \cdot 7H_2O$ | 49 | 7 | 7 |

[a] Reactions were carried out by stirring a mixture of benzaldehyde (10 mmol), cyclohexanone (10 mmol), $HC(OCH_3)_3$ (12 mmol) and catalyst (0.1 mmol) in methanol (5 $cm^3$) at 20 °C for 30 min. The yields were determined by GLC.
[b] $PhCH(OCH_3)_2/C_6H_{10}(OCH_3)_2$.

**Table 3** Catalytic activity of lanthanoid trifluoromethanesulfonates, $Ln(OTf)_3$

| | Yields of acetals[a] (%) | |
|---|---|---|
| Ln | $PhCHO^{b}$ | $PhCOCH_3{}^{c}$ |
| La | 47 | 22 |
| Sm | 72 | 31 |
| Gd | 75 | 47 |
| Er | 78 | 52 |
| Yb | 84 | 69 |

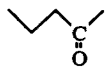
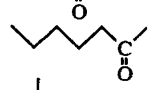
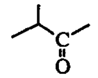
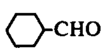
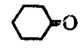
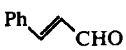
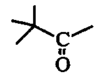
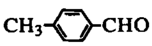
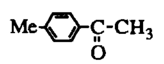
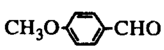
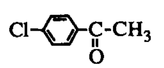
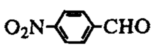
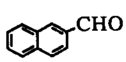
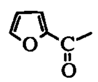
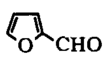
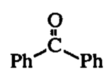
[a] Yields were determined by GLC using internal standards.
[b] Reaction conditions: PhCHO (5 mmol), $HC(OCH_3)_3$ (10 mmol), catalyst (0.025 mmol), methanol (5 $cm^3$), at 0 °C for 5 min.
[c] Reaction conditions: $PhCOCH_3$ (5 mmol), $HC(OCH_3)_3$ (10 mmol), catalyst (0.05 mmol), methanol (5 $cm^3$), at 30 °C for 1 h.

acetal to cyclohexanone dimethyl acetal were around 5:1 and were equal to those obtained in the reaction by the chloride catalyst. Therefore, the chemoselectivity of the sulfonates is estimated to be as high as that of the chloride.

The effect of lanthanoid metals on catalytic activity was examined in the acetalization using $Ln(OTf)_3$, which was the most reactive. The results are summarized in Table 3. In the acetalization of benzaldehyde, the catalytic activity of $Ln(OTf)_3$ increased steadily with the atomic number of the lanthanoid. This trend was also observed in the acetalization of acetophenone. Additionally, $YbCl_3$ and $Yb(OCas)_3$ were more catalytically active than the corresponding lanthanum compounds as seen in Table 1. These facts indicate that catalytic activity increases in inverse proportion to the ionic radius of the lanthanoid metals. Since the lanthanoid metals are hard elements, the decrease in the radius simply results in an increase in the acidity towards hard bases. The increase in the acidity of the catalysts is deduced to bring about the enhancement of catalytic activity. Consequently, this acetalization is considered to be an acid-catalyzed reaction. In fact, the complementary effect on lanthanoid metals is known in base-catalyzed reactions using lanthanoid complexes.[5] On the basis of this deduction, the catalytic activity of $YbX_3$ [$X = CF_3SO_3 > p\text{-}CH_3C_6H_4SO_3 > Cl > 2,4,6\text{-}(NO_2)_3C_6H_2O$] can be accounted for by the acidity of metal center depending on the electron-withdrawing property of X.

The acetalizations of various aldehydes and ketones were carried out using $Yb(OTf)_3$ as a

**Table 4** Acetalization of carbonyl compounds with methyl orthoformate in the presence of $Yb(OTf)_3$ in methanol

| Aldehyde[a] | Yield[b] (%) | Ketone[c] | Yield[b] (%) |
|---|---|---|---|
|  | 86 |  | 95 |
|  | 92 |  | 96 |
|  | 98 |  | 96 |
|  | 99 |  | 97 |
|  | 93 |  | 37 |
|  | 91 |  | 98 |
|  | 95 |  | 97 |
|  | 11 | | |
|  | 97 |  | 98 |
|  | 96 |  | 9 (96)[d] |

Reaction conditions: carbonyl compound (5 mmol), $HC(OCH_3)_3$ (10 mmol), $Yb(OTf)_3$ (0.05 mmol) in methanol (5 $cm^3$).
[a] At 20 °C for 30 min.
[b] Determined by GLC using internal standards.
[c] At 40 °C for 3 h.
[d] Reflux for 24 h.

catalyst. The results are summarized in Table 4. Aldehydes were readily acetalized at 20 °C for 30 min to give the corresponding acetals in high yields. Though ketones were less reactive, the quantitative acetalizations were achieved at 40 °C for 3 h, except for ketones having bulky substituents. However, benzophenone could be acetalized almost quantitatively at a higher temperature.

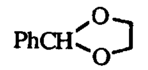
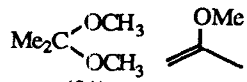
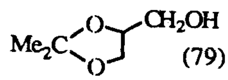
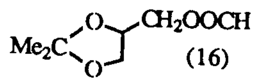
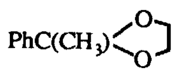
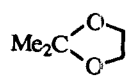
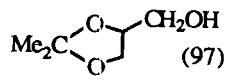
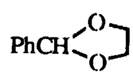
Methanol is not a good solvent for the acetalization of highly lipophilic compounds, which are not so soluble in methanol solutions containing salts such as lanthanoid chlorides. We took advantage of the high solubility of $Yb(OTf)_3$ and $Yb(OCas)_3$ to attempt the acetalization in an ether or dichloromethane solution containing water (0.6 vol%). Benzaldehyde was readily reacted with methyl orthoformate in either solvent to give the dimethyl acetal in a high yield (see Table 5). Acetone also gave the acetal in a good yield, though a small amount of 2-methoxypropene was by-produced.

Cyclic acetals, which are the most widely used for the protection of carbonyl groups, could also be prepared by this acetalization in the presence of polyols. For example, the reactions of benzaldehyde and acetophenone with methyl orthoformate and ethylene glycol gave the corresponding 1,3-dioxolanes in high yields. The reaction of actone in the presence of glycerol formed 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane in 79% yield. In this reaction, the corresponding 1,3-dioxane compound was not detected, whereas a small amount of the formate of the 1,3-dioxolane was formed. The goal in obtaining the pure 1,3-dioxolane was provided by the reaction of acetone dimethyl acetal with glycerol. 4-Hydroxymethyl-1,3-dioxolane is an important starting material for organic synthesis. Therefore, the asymmetric synthesis of this compound was attempted by use of the ytterbium camphorsulfonate. This catalyst was active enough for the reaction of acetone dimethyl acetal with glycerol under mild conditions, but the optical yield of the 1,3-dioxolane was unfortunately very low. This type of exchange reaction with $Yb(OTf)_3$ was also applicable to the reaction of benzaldehyde dimethyl acetal with ethylene glycol, butanol or ethanol. Interestingly, diethyl carbonate also

[2]

| Reaction conditions | Isolated yield (%) | Optical yield |
|---|---|---|
| 20 °C for 2 h | 63 | 0.5 |
| 0 °C for 20 h | 42 | 1.5 |

**Table 5** Various acetalizations catalyzed by $Yb(OTf)_3$

| Substrate | Reagents | Reaction conditions[a] | Products (yield, %)[b] |
|---|---|---|---|
| Benzaldehyde | $HC(OCH_3)_3$ | Reflux for 1 h in ether (5 $cm^3$)[c] | Benzaldehyde dimethyl acetal (96) |
| Benzaldehyde[d] | $HC(OCH_3)_3$ | Reflux for 1 h in ether (5 $cm^3$)[c] | Benzaldehyde dimethyl acetal (94) |
| Benzaldehyde | $HC(OCH_3)_3$ | Reflux for 1 h in $CH_2Cl_2$ (5 $cm^3$)[c] | Benzaldehyde dimethyl acetal (96) |
| Benzaldehyde | $HC(OCH_3)_3$ $HOCH_2CH_2OH$ | 20 °C, 1 h |  (93) |
| Acetone | $HC(OCH_3)_3$ | Reflux for 1 h in ether (5 $cm^3$)[c] |  (81) (19) |
| Acetone | $HC(OCH_3)_3$ + glycerol | 40 °C, 1 h |  (79)  (16) |
| Acetophenone | $HC(OCH_3)_3 + HOCH_2CH_2OH$ | 40 °C, 1 h |  (87) |
| Acetone dimethyl acetal | $HOCH_2CH_2OH$ | 40 °C, 1 h |  (95) |
| Acetone dimethyl acetal | Glycerol | 40 °C, 1 h |  (97) |
| Benzaldehyde dimethyl acetal | $HOCH_2CH_2OH$ | 20 °C, 1 h |  (89) |
| Benzaldehyde dimethyl acetal | Butanol | 20 °C, 1 h in BuOH (5 $cm^3$) | Benzaldehyde dibutyl acetal (84) |
| Benzaldehyde dimethyl acetal | Ethanol | 20 °C, 1 h in EtOH (5 $cm^3$) | Benzaldehyde diethyl acetal (92) |
| Benzaldehyde dimethyl acetal | $(EtO)_2CO$ | 100 °C, 70 h in $(EtO)_2CO$ (5 $cm^3$) | Benzaldehyde diethyl acetal (83) |

[a] A mixture of substrate (5 mmol), reagents (10 mmol) and $Yb(OTf)_3$ (0.5 mmol) was used.
[b] GLC yields using an internal standard.
[c] Water (0.03 $cm^3$) was added.
[d] $Yb(OCas)_3 \cdot \frac{1}{2}THF$ (0.05 mmol) was used instead of $Yb(OTf)_3$.

reacted with benzaldehyde dimethyl acetal, which gave the diethyl acetal in good yield, although severe reaction conditions were required. This fact suggests that the ytterbium compound is able to catalyze the exchange reaction of the alkoxyl group of esters. The details of the ester exchange reaction are now under investigation.

## EXPERIMENTAL

### General comments

All operations were performed using Schlenk tube techniques under argon atmosphere. Methanol, ethanol and butanol were distilled from the corresponding magnesium alkoxide.

Ether and THF were distilled from sodium benzophenone ketyl. Dichloromethane was refluxed over calcium hydride and distilled. Trifluoromethanesulfonic acid, *p*-toluenesulfonic acid, (1*S*)-10-camphorsulfonic acid, 2,4,6-trinitrophenol and the other solid chemicals were used as received. The other liquid organic chemicals were purified by distillation before use. $Yb(Pic)_3 \cdot 8H_2O$[6] was prepared according to the published procedure. $Ln(OTf)_3$ was obtained by dehydrating $Ln(OTf)_3 \cdot nH_2O$, which was prepared using the reaction of $Ln_2O_3$ with 3 equiv of trifluoromethanesulfonic acid in water[7] and purified by a recrystallization from water. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-GX 270 spectrometer at 270 and 67.8 MHz, respectively. Gas-chromatographic analyses were performed on a Yanagimoto G-2800 with a flame ionization detector using naphthalene or durent as an internal calibrant.

## Preparation of $Yb(OTs)_3 \cdot 9H_2O$

A mixture of $Yb_2(CO_3)_3$ (1.58 g, 3 mmol) and *p*-toluenesulfonic acid (3.44 g, 20 mmol) in 20 $cm^3$ of water was refluxed for 30 min. The solution was filtered and concentrated to dryness under reduced pressure. A colorless solid was recrystallized twice from a THF solution containing small amounts of water (1–2 vol%). Colorless crystals were collected and dried under reduced pressure at room temperature. Yield: 2.3 g (45%). M.p. >300°C. IR (KBr): $\nu$ 1170 (s), 1128 (m), 1043 (m) $cm^{-1}$.

Analysis: calcd for $C_{21}H_{39}O_{15}S_3Yb$: C, 29.72; H, 4.63. Found: C, 29.71; H, 4.55%.

## Preparation of $Yb(OCas)_3 \cdot \frac{1}{2}$ THF

To a mixture of (1*S*)-10-camphorsulfonic acid (4.65 g, 20 mmol), water (1.5 $cm^3$) and THF (40 $cm^3$) was added portionwise $Yb_2(CO_3)_3$ (1.58 g, 3 mmol) with stirring. After refluxing for 30 min, the clear solution was filtered and cooled with ice. Methyl orthnoformate (10 $cm^3$) was added dropwise to the cold solution, and the mixture was allowed to stand at room temperature for 20 h to give colorless crystals. The crude crystals collected were suspended in 30 $cm^3$ of refluxing THF, and water (about 1 $cm^3$) was added to the suspension until it became clear. The solution was cooled with ice, and then methyl orthoformate (10 $cm^3$) was added dropwise to the solution. Colorless crystals deposited at room temperature after 20 h were collected, washed with THF and dried at 110 °C under reduced pressure. Yield: 3.09 g (57%). M.p. >300 °C. $[\alpha]_D^{20}+15.9°$ ($c$=2.0in $H_2O$).

IR (KBr): $\nu$ 1738 (s), 1165 (s), 1083 (s) $cm^{-1}$.

Analysis: calcd for $C_{64}H_{98}O_{25}S_6Yb_2$: C, 42.56; H, 5.46. Found: C, 42.50; H, 5.60%.

## Preparation of $La(OCas)_3 \cdot \frac{1}{2}$THF

This compound was prepared from $Yb_2(CO_3)_3$ (1.58 g, 3 mmol) in a similar way to $Yb(OCas)_3 \cdot \frac{1}{2}$THF. This was less soluble than the Yb analogue in aqueous THF. Yield: 3.39 g (65%). M.p. >300 °C. $[\alpha]_D^{20}-141°$ ($c$=2.0 in $H_2O$).

IR (KBr): $\nu$ 1738 (s), 1155 (s), 1048 (s) $cm^{-1}$. $^1H$ NMR ($D_2O$, 27 °C): $\delta$ 3.27 (d, $J$=15 Hz, 1H), 2.85 (d, $J$=15 Hz, 1H), 2.4 (m, 2H), 2.15 (t, $J$=4.5 Hz, 1H), 2.0 (m, 2H), 1.63 (ddd, $J$=13.9, 9.5, 4.5 Hz, 1H), 1.45 (ddd, $J$=12.2, 9.5, 3.8 Hz, 1H), 1.03 (s, 3H), 0.82 (s, 3H), except for THF. $^{13}C$ NMR ($D_2O$, 27 °C) $\delta$ 222.6, 59.0, 48.7, 43.2, 42.8, 26.7, 25.9, 19.4, 19.3.

Analysis: calcd for $C_{64}H_{98}O_{25}S_6La_2$: C, 44.23; H, 5.69. Found: C, 44.16; H, 5.71%.

## Acetalization

A typical experiment was carried out as follows. A solution of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and methyl orthoformate (1.06 g, 10 mmol) in methanol (5 $cm^3$) was stirred at 20 °C, and then an aldehyde (5 mmol) was added. After stirring at 20 °C for 30 min, the reaction mixture was poured into a mixture of 5% aqueous $NaHCO_3$ solution (5 $cm^3$), ether (10 $cm^3$) and naphthalene or durene as an internal cariblant. The ether layer was separated and dried over anhydrous $K_2CO_3$. The acetal in the ether solution was quantitatively analyzed by means of gas chromatography.

## 2,2-Dimethyl-4-hydroxymethyl-1,3-dioxolane

A mixture of glycerol (9.21 g, 0.1 mol), acetone dimethyl acetal (5.21 g, 0.05 mol) and $Yb(OCas)_3 \cdot \frac{1}{2}$THF (401 mg, 0.5 mmol) was stirred at 0 °C for 20 h. After addition of approximately 10 g of anhydrous $K_2CO_3$ to the reaction mixture, the product was extracted twice with 50 $cm^3$ portions of ether. The extract was washed with a little water, and then dried over anhydrous $K_2CO_3$. After filtration and concentration of the ether solution, the oily residue was distilled under a reduced pressure to give 2.8 g of the dioxolane (yield 42%, b.p. 100–102 °C/25 mmHg). $[\alpha]_D^{20}$ −0.2° ($c = 15$ in benzene). The optical yield (1.5%) was determined on the basis of the literature value of the optical rotation.[8]

$^1$H NMR ($CDCl_3$, 27 °C): $\delta$ 4.21 (m, 1H), 4.04 (dd, $J = 8.3$, 6.5 Hz, 1H), 3.78 (dd, $J = 8.0$, 6.5 Hz, 1H), 3.72 (dd, $J = 11.5$, 5.3 Hz, 1H), 3.59 (dd, $J = 11.6$, 5.1 Hz, 1H), 3.25 (s, 1H), 1.43 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR ($CDCl_3$, 27 °C): $\delta$ 109.4, 76.4, 66.0, 63.1, 26.6, 25.3.

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