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Note

A novel application of tin-based alkoxide anion for deacetylation

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Abstract

A stannylene acetal, in the presence of CsF, is able to cleave both aromatic and aliphatic acetates rapidly and efficiently under room temperature. Control experiments indicate that both the stannylene acetal and CsF are required and play significant roles in the deacetylation process. Thus, it is likely that the tin-based alkoxide anion generated by a stannylene acetal and CsF is responsible for deacetylation.

Keywords: Stannylene acetal; Cesium fluoride; Alkoxide anion; Deacetylation

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1. Introduction

Dibutylstannylene acetals have been broadly employed to prepare monoprotection and further functionalization of diols and carbohydrates [1–8]. However, we report herein, for the first time, that a stannylene acetal, in the presence of CsF, is able to cleave both aromatic and aliphatic acetates rapidly and efficiently under room temperature. Control experiments indicate that both the stannylene acetal and CsF are required and play significant roles in the deacetylation process. Thus, it is likely that the tin-based alkoxide anion generated by a stannylene acetal and CsF is responsible for deacetylation.

2. Results and discussion

We reasoned that alkoxide anions generated from dibutylstannylene acetals are highly reactive, in conjunction with our earlier work on alkylation of ecdysteroid [9], we decided to investigate whether highly reactive dibutylstannylene acetals could remove acetyl group to furnish free alcohols under mild conditions efficiently in the presence of a nucleophile such as CsF. To test this notion, a series of simple aromatic and aliphatic acetates (containing an aromatic moiety for convenience of monitoring the reaction progress by TLC under UV light) were treated with 2,2-dibutyl-[1,3,2]dioxastanninane **1** in the presence of CsF (Table 1), a nucleophile that is believed to promote dibutylstannylene acetal-based reactions [10]. 2,2-dibutyl-[1,3,2]dioxastanninane **1** was readily prepared *in situ* by treating dibutyltin oxide and 1,3-propanediol in refluxing methanol for 3 h followed by sequential removal of methanol and any remaining water as a benzene azeotrope. The resulting **1** was used for deacetylation without further purification. Both aromatic (substrates **2**–**7**) and aliphatic (substrates **8**–**13**) acetates react rapidly with **1** and CsF in DMF at room temperature to afford the corresponding alcohols (**2**–**13**) in excellent yields after silica gel column chromatography. TLC analysis indicated that the reaction was essentially complete within 1 h. The electron withdrawing and donating groups, as well as sterically crowded substituents on the aromatic rings have no apparent effect on the deacetylation reaction.

To determine whether the above deacetylation reaction by 2,2-dibutyl-[1,3,2]dioxastanninane **1** and CsF was a radical or non-radical based mechanism, the deacetylation reaction was conducted in the presence of **1**, CsF, and a radical inhibitor, *p*-dinitrobenzene, we did not observe markedly changes of either reaction rate or yield. This supports

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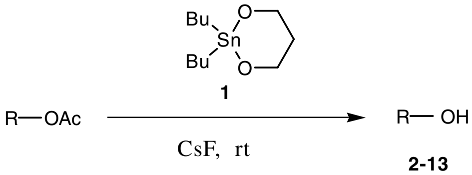
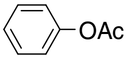
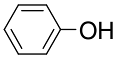
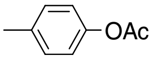
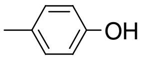
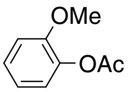
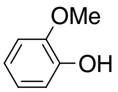
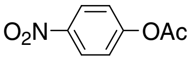
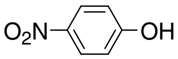
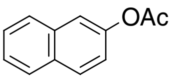
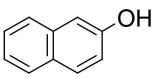
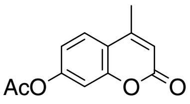
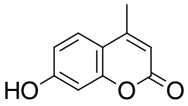
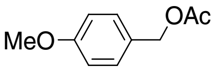
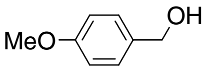
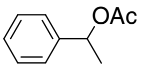
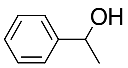
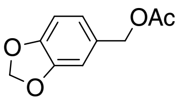
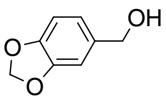
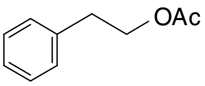
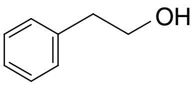
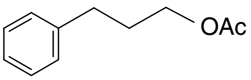
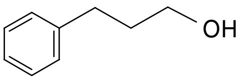
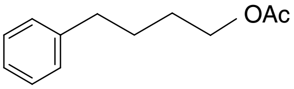
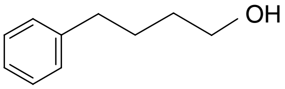
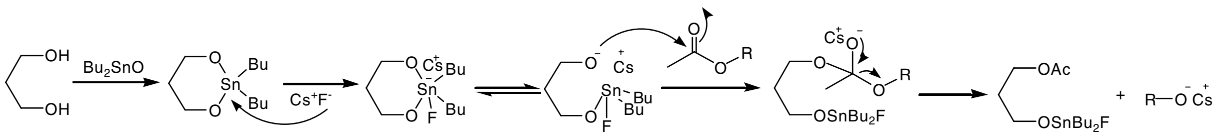
a non-radical mechanism. Furthermore, when the acetates were treated with dibutyltin oxide (instead of **1**) and CsF in the absence of 1,3-propanediol, or when the acetates were treated with 2,2-dibutyl-[1,3,2]dioxastanninane **1** in the absence of CsF, the deacetylation reaction proceeded at a much slower rate, the deacetylation reaction barely occurred (less than 5% product formed) after overnight. In addition, when the acetates were treated with CsF alone, the deacetylation reaction did not occur. These control experiments indicate that both **1** and CsF are required and play significant roles in the deacetylation process. A plausible mechanism for the deacetylation by 2,2-dibutyl-

Table 1
Deacetylation of aromatic and aliphatic acetates with 2,2-dibutyl-[1,3,2]dioxastanninane **1** and CsF at room temperature



Acetate	Reaction time (h)	Isolated yield (%)	Product	Product no.
	1	85		2
	1	84		3
	0.5	90		4
	1	92		5
	0.5	98		6
	0.5	85		7
	0.5	83		8
	0.5	84		9
	1	83		10
	0.5	85		11
	0.5	92		12
	1	95		13



Scheme 1.

[1,3,2]dioxastanninane **1** and CsF is outlined in Scheme 1. Dibutyltin oxide initially condenses with 1,3-propanediol to give **1**. The added nucleophile, fluoride is believed to promote dibutylstannylene acetal-based reactions by attacking the tin atom of **1** to form a pentacoordinated intermediate, which equilibrates a highly reactive alkoxide anion [10]. Nucleophilic attack by the alkoxide anion on the electrophilic carbon of acetates should then remove the acetyl group to furnish the free hydroxyl-bearing products.

3. Conclusions

In summary, in conjunction with CsF, a stannylene acetal **1**, has been shown able to deacetylate rapidly (less than 1 h) and efficiently (over 80%) both aromatic and aliphatic acetates under very mild conditions (room temperature). Control experiments indicate that both the stannylene acetal and CsF are required and play significant roles in the deacetylation process. The deacetylation reaction likely proceeds by a non-radical transesterification mechanism via a highly reactive fluoride-generated tin-based alkoxide anion. This novel application of tin-based alkoxide anion for deacetylation should open a new avenue for the further developments of tin chemistry.

4. Experimental

4.1. Typical experimental procedure

A suspension of dibutyltin oxide (200 mg, 0.803 mmol) and 1,3-propanediol (47 mg, 0.617 mmol) in anhydrous methanol (12 ml) was heated to reflux for 3 h under argon. After the solvent was removed under reduced pressure, the residue was subsequently azeotroped with anhydrous benzene. To the resulting 2,2-dibutyl-[1,3,2]dioxastanninane **1**, CsF (94 mg, 0.617 mmol), aromatic or aliphatic acetates (0.474 mmol), 3 Å molecular sieves (100 mg), and anhydrous DMF (2 ml) were added. The reaction mixture was stirred at room temperature for 0.5–1 h, and then the reaction was quenched by addition of brine. After extraction three times with ethyl acetate, the combined organic phases were dried over Na_2SO_4, filtered through a glass funnel and concentrated. Purification by flash column chromatography (methylene chloride/methanol: 1/20) furnished the alcohol (**2**–**13**).

Compound **2**: ^1H NMR (300 MHz, CD_3OD, TMS): δ 7.1–7.18 (m, 2H), 6.75–6.82 (m, 3H); MS (EI) *m*/*z* 94 (M^+).

Compound **3**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.24 (d, 2H), 6.94 (d, 2H), 4.82 (s, 1H), 2.48 (s, 3H); MS (EI) *m*/*z* 108 (M^+).

Compound **4**: ^1H NMR (300 MHz, CD_3OD, TMS): δ 6.85–6.89 (m, 1H), 6.74–6.80 (m, 3H), 3.81 (s, 3H); MS (EI) *m*/*z* 124 (M^+).

Compound **5**: ^1H NMR (300 MHz, CD_3OD, TMS): δ 8.06–8.11 (m, 2H), 6.83–6.88 (m, 2H); HRMS calc. for $C_6H_6NO_3$ $(M+H)^+$, 140.0348; found, 140.0354.

Compound **6**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 8.00–7.88 (m, 3H), 7.65–7.58 (m, 2H), 7.36–7.30 (m, 2H), 5.32 (s, 1H); HRMS calc. for $C_{10}H_8O$ (M^+), 144.0575; found,144.0577.

Compound **7**: ^1H NMR (300 MHz, CD_3OD, TMS): δ 7.58 (d, 1H), 6.83 (d, 1H), 6.69 (d, 1H), 6.09 (s, 1H) 2.42 (s, 3H); HRMS calc. for $C_{10}H_9O_3$ $(M+H)^+$, 177.0552; found, 177.0554.

Compound **8**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.47 (d, 2H), 7.09 (d, 2H), 4.80 (s, 2H), 4.00 (s, 3H), 2.00 (s, 1H); HRMS calc. for $C_8H_{10}O_2$ (M^+), 138.0681; found, 138.0683.

Compound **9**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.46–7.59 (m, 5H), 5.08 (t, 1H), 2.22 (s, 1H), 1.69 (d, 3H); MS (FAB) *m*/*z* 105 $(M-H_2O+H)^+$.

Compound **10**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.05 (s, 1H), 6.98 (d, 2H), 6.14 (s, 2H), 4.75 (s, 2H), 2.20 (s, 1H); HRMS calc. for $C_8H_8O_3$ (M^+), 152.0473; found, 152.0473.

Compound **11**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.25–7.34 (m, 2H), 7.21–7.25 (m, 3H), 3.84 (t, 2H), 2.86 (t, 2H), 2.05 (s, 1H); HRMS calc. for $C_8H_{10}O(M^+)$, 122.0732; found, 122.0749.

Compound **12**: ^1H NMR (300 MHz, CD_3OD, TMS): δ 7.29–7.21 (m, 2H), 7.21–7.11 (m, 3H), 3.59 (t, 2H), 2.70 (t, 2H), 2.56 (s, 1H), 1.81–1.91 (m, 2H); MS (EI) *m*/*z* 136 (M^+).

Compound **13**: ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.29–7.19 (m, 2H), 7.19–7.12 (m, 3H), 3.58 (t, 2H), 2.63 (t, 2H), 1.98 (s, 1H), 1.53–1.74 (m, 4H); MS (EI) *m*/*z* 150 (M^+).

Acknowledgments

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