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Acylative Dimerization of Tetrahydrofuran Catalyzed by Rare-Earth Triflates

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ABSTRACT

Ytterbium, scandium, and lanthanum triflates catalyze the cleavage reactions of cyclic ethers to give various products. Most notable was the acylative cleavage of tetrahydrofuran with acetic anhydride catalyzed by Yb(triflate)₃ to give the dimeric compound $CH_3CO_2(CH_2)_4O(CH_2)_4$ OCOCH₃ in 69% yield.

Key Words: Lewis acids; Tetrahydrofuran; Rare-earth triflates.

1871

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INTRODUCTION

Various Lewis acids and transition metals catalyze the cleavage of tetrahydrofuran into monomeric difunctional products such as 4-halobutyl alkanoates,^[1-5] 4-halobutyl alcohols,^[5] and TMS ethers of 4-phenylseleno alcohols.^[6] A handful of reactions give difunctional products incorporating two tetrahydrofurans. For example, the cleavage of tetrahydrofuran with phosphorus oxychloride catalyzed by sulfuric acid gave the dimeric product 1-chloro-4-(4-chlorobutoxy)butane in 70% yield.^[7] Acetic anhydride cleavage of tetrahydrofuran catalyzed by HClO₄,^[8] heteropolytungstic acids,^[9] or montmorillonite-type earth^[10] gave good yields of the dimeric product 4-(4-acetoxybutoxy)butyl acetate (1a) using excess acetic anhydride. Stoichiometric TiCl₄ and excess THF gave 1-chloro-4-(4-chlorobutoxy)butane in 55% yield.^[11] Conditions leading to the polymerization of tetrahydrofuran to give poly(tetramethylene oxide)^[12] also has been intensely investigated, since polymers and block copolymers of tetrahydrofuran are important commercial products (e.g., spandex fibers). Polymerization catalysts such as oxonium ions^[13] and triflate esters^{<math>[14]} are typically used to initiate the cationic</sup></sup> polymerization.

Given the importance of the cleavage reactions of cyclic ethers, it is not surprising that rare-earth metal triflates,^[15] a newly emerging class of Lewis acids, have been investigated as catalysts for ether cleavage reactions. The rare-earth metal triflates are remarkably active Lewis acids, and are useful water-tolerant, potentially recyclable catalysts in such diverse reactions as the Diels-Alder, Michael, aldol, Friedel-Crafts, and Baeyer-Villiger reactions.^[15] The studies employing rare-earth metal triflates and related complexes in ether cleavage reactions have, for the most part, looked at cleavage reactions of acyclic ethers used as protecting groups. Several highly chemoselective methods for the cleavage of trityl,^[16] TBS,^[17] prenyl,^[18] MOM,^[19] and benzylic ethers^[20,21] using rare-earth metal catalysts have been developed. Scandium triflate is an effective catalyst for the direct conversion of O-trimethylsilyl cyanohydrins into the respective O-acetyl cyanohydrins.^[22] The rare-earth metal triflates also are effective catalysts for the ring-opening reactions of highly strained epoxides and oxetanes giving monomeric products,^[15] but the only reports in the literature concerning the cleavage reactions of tetrahydrofurans has been in their role as catalysts leading to polymeric materials.^[23,24] Since these studies indicated the facile cleavage of cyclic ethers using rare-earth triflates, we decided to examine the acylative cleavage reactions of tetrahydrofuran catalyzed by ytterbium, scandium, or lanthanum triflate under conditions favoring low molecular weight products.

When a 2.3 : 1 molar mixture of tetrahydrofuran and acetic anhydride was heated $(80-85^{\circ}C, 0.5 \text{ hr})$ with ytterbium triflate (4 mol%), the crude product

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contained dimeric AcO(CH₂)₄O(CH₂)₄OAc (1a) as the major product (\sim 60%), along with AcO(CH₂)₄OAc (2a; 5%), AcO(CH₂)₄O(CH₂)₄O(CH₂)₄OAc (3a; 25%), and higher oligomers (Sch. 1). With a routine extractive workup procedure, we obtained 40-50% isolated yields of 1a. The isolated yield of 1a improved markedly with two variations: direct distillation of the reaction mixture after addition of Na₄EDTA and/or careful addition of THF to the acetic anhydride/catalyst mixture. Distillation directly from the reaction flask takes advantage of the conversion of 3a (and higher oligomers) to 1a (69% isolated yield; Table 1). The addition of Na₄EDTA moderates the activity of $Yb(OTf)_3$ so that the formation of monomeric 2a is minimized. Optimal crude yield of 1a (1a: 2a: 3a; 75: 10: 15) requires the careful balance of catalyst activation, catalyst concentration, addition rate of THF, and temperature (see Experimental) so that the THF concentration is not too low, which promotes the formation of monomeric 2a, nor too high, which favors 3a and higher oligomers. Various additives or solvents were tried, but they either did not influence selectivity and yield (CH₃NO₂) or they deactivated the catalyst (NaHCO₃ and CH₃CN). The wetness of the THF was only a minor determinant of yield or selectivity, since the addition of unpurified THF containing 5 mol% water gave only slightly diminished yields (54%) of isolated 1a. Scandium triflate gave comparable but more variable (55-70%) yields of 1a, and lanthanum triflate gave lower (55%) yields of 1a. Although watersoluble rare-earth triflates are potentially recoverable, we were unable to develop efficient procedures for separating the catalyst from the products. When triflic acid (4 mol%) was used under similar conditions, 1a was isolated in 52% yield. Perchloric acid-catalysis (4 mol%) of the reaction of THF with acetic anhydride^[8] required much longer reaction times and gave lower yields of 1a.

The reaction of tetrahydrofuran with several other anhydrides-propionic, chloroacetyl, benzoic, and crotonoic-gave fair to good yields of the respective dimeric products 1 (Table 1) using conditions similar to the conditions



Scheme 1.

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Anhydride	Catalyst	Product (%yield)
(CH ₃ CO) ₂ O	Yb(OTf) ₃	CH ₃ CO ₂ (CH ₂) ₄ O(CH ₂) ₄ OCOCH ₃ , 1a (65–69) CH ₃ CO ₂ (CH ₂) ₄ OCOCH ₃ , 2a (10–15)
$(CH_3CO)_2O$	Sc(OTf) ₃	1a (55–70)
(CH ₃ CO) ₂ O	La(OTf) ₃	1a (55)
(CH ₃ CO) ₂ O	HOTf	1a (52)
$(CH_3CO)_2O$	HClO ₄	1a (21)
(CH ₃ CH ₂ CO) ₂ O	Yb(OTf) ₃	CH ₃ CH ₂ CO ₂ (CH ₂) ₄ O(CH ₂) ₄ OCOCH ₂ CH ₃ ,
		1b (59)
$(ClCH_2CO)_2O$	Yb(OTf) ₃	ClCH ₂ CO ₂ (CH ₂) ₄ O(CH ₂) ₄ OCOCH ₂ Cl, 1c (42)
$(C_6H_5CO)_2O$	Yb(OTf) ₃	$C_6H_5CO_2(CH_2)_4O(CH_2)_4OCOC_6H_5$ 1d (58)
$(CH_3CH=CHCO)_2O$	Yb(OTf) ₃	$CH_3CH = CHCO_2(CH_2)_4O(CH_2)_4OCOCH =$
· · · · ·		CHCH ₃ , 1e (56)

Table 1. Reaction of tetrahydrofuran with anhydrides.

1874

developed for the Yb(OTf)₃-catalyzed reaction of tetrahydrofuran with acetic anhydride. Yb(OTf)₃ catalyzed the polymerization of methacrylic anhydride under these conditions, and we were unable to develop alternate conditions leading to appreciable amounts of 1. We briefly looked at other cyclic ethers under the reaction conditions described for the acylative dimerization of tetrahydrofuran, but these reactions were not as interesting or useful as the cleavage reactions of tetrahydrofuran. The Yb(OTf)3-catalyzed reaction of 2-methyltetrahydrofuran with acetic anhydride gave monomeric AcO(CH₂)₃ CH(CH₃)OAc in 47% yield, whereas the analogous reaction employing Sc(OTf)₃ catalysis gave a mixture of 4-penten-1-yl acetate, (E)-3-penten-1-yl acetate, and (Z)-3-penten-1-yl acetate with low yields of the dimeric diester. The slow reaction of tetrahydrofuryl acetate and acetic anhydride using Sc(OTf)₃ catalysis gave 1,2,5-triacetoxypentane, similar to the reaction employing HClO₄ catalysis. Tetrahydropyran and dioxane reacted slowly with acetic anhydride (4 mol% Yb(OTf)₃) to give low yields of complex mixtures. The acylative ring-opening reactions of oxetane catalyzed by Yb(OTf)₃ gave oligomeric compounds.

In order to probe the origin for the selectivity of the dimeric diester 1, we performed several control and crossover experiments. When the diester 1a was heated with Yb(OTf)₃ (4 mol%) at 85°C for 2 hr, it was recovered unchanged. ¹H NMR studies indicated that an equimolar mixture of diester 1a and acetic anhydride with Yb(OTf)₃ (4 mol%) heated for 2 hr at 85°C also was unchanged. When 1a is heated to 140°C in the presence of Yb(OTf)₃ (4 mol%), however, we do see the formation of THF and monomeric 2a, consistent with our observations of the distillation of the



crude reaction mixtures and with the observations by Drysdale in the depolymerization of polytetrahydrofuran.^[23] When aliquots are removed during the addition of THF to acetic anhydride using Yb(OTf)₃ (4 mol%), the ratio of 1a: 2a: higher oligomers does not change substantially. These control experiments rule out an equilibrium process favoring 1a, as has been proposed for the related reaction of THF with phosphorous oxychloride,^[7] although there is significant equilibration of the products in the presence of the rare-earth catalysts at the temperatures necessary for distillation. The control experiments employing a rare-earth catalyst were in stark contrast to the results we obtained employing triflic acid (4 mol%) as the catalyst: the ratio of 1a: 2a: higher oligomers changed significantly during the course of the reaction, with greater than 60% yield of higher oligomers at 50% conversion of THF (15 min) to a final product ratio of 25:60:15 (2 hr). We also observed significant conversion of dimer 1a to monomer 2a under the standard reaction conditions employing triflic acid (4 mol%, 80°C), which we feel is strong evidence for equilibrium control for the triflic acid-catalyzed reaction. In a crossover experiment, the addition of THF to an equimolar mixture of acetic and propionic anhydride with Yb(OTf)₃ or Sc(OTf)₃ catalysis gave nearly a statistical mixture of the three possible diesters $(1a: AcO(CH_2)_4O(CH_2)_4)$ $OCOCH_2CH_3$: **1b**; 1:2:1). This crossover experiment rules out a mechanism in which both THF molecules and the anhydride form 1 entirely within the coordination sphere of only one rare-earth metal.

We propose the following mechanism for the selectivity of the dimer in the rare-earth catalyzed reactions of tetrahydrofuran with anhydrides (Sch. 2). The activation of anhydrides for Friedel-Crafts reactions and esterification reactions is well documented, so the rare-earth catalyst plays a pivotal role in the first step of the mechanism, the acylation of tetrahydrofuran to give acyl cation 4. Nucleophilic attack by a carboxylate anion on intermediate 4 leads to monomeric product 2, whereas nucleophilic attack by another tetrahydrofuran within the coordination sphere of the Lewis acidic rare-earth metal leads to oxonium ion 5. As in the case of intermediate 4, oxonium ion 5 can undergo nucleophilic attack by a carboxylate anion to give dimeric product 1 or by another tetrahydrofuran to give oxonium ion 6 that ultimately leads to trimeric product 3 or higher oligomers. The proposed mechanism, in which the rare-earth metal acts as a template for the addition of the second THF (coordination number is unknown and shown for illustration purposes only), is based on the proposed mechanisms for the polymerization of THF,^[12] the reaction of TiCl₄ with THF to give 1-chloro-4-(4-chlorobutoxy)butane,^[11] and the TiCl₄ oligomerization of THF in the presence of acetyl chloride or epichlorohydrin.^[25] Further studies will provide a firmer basis for defining the mechanism for this reaction.

The rare-earth metal triflate-catalyzed acylative dimerization of tetrahydrofuran is an attractive method for the synthesis of dimeric diesters **1**. The

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traditional two-step synthesis of **1a** (57% overall yield) based on the cleavage of tetrahydrofuran with phosphorus oxychloride generates obnoxious byproducts. The synthesis of **1** presented in this paper is "green": no byproducts. The previous report using heteropoly acids such as $H_3PW_{12}O_{40}$ to give dimeric diester **1a** requires a high Ac₂O: THF ratio at incomplete conversions,^[9] whereas the rare-earth catalyzed reaction described here can be conducted at nearly the desired stoichiometric ratio. We are continuing to investigate the interesting mechanistic questions posed by this study and are exploring conditions that will allow for the recovery of the rare-earth catalyst. These studies and the synthesis of unique polymers will be reported in due course.

EXPERIMENTAL

All reactions were carried out under Ar. IR spectra were obtained on a Perkin Elmer 1600 Series FT-IR spectrometer. The ¹H and ¹³C NMR spectra







were recorded at 400 and 100 MHz, respectively, on a JEOL Eclipse+400 spectrometer; all chemical shifts are reported in ppm relative to TMS ($\delta = 0.00$ ppm) in the proton NMR and relative to CDCl₃ ($\delta = 77.0$ ppm) in the carbon NMR. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh). Elemental analyses were performed by Galbraith Laboratories, Inc. Ytterbium trifluoromethanesulfonate hydrate (Yb(OTf)₃), scandium trifluoromethanesulfonate (Sc(OTf)₃), and lanthanum trifluoromethanesulfonate (La(OTf)₃) were purchased from Aldrich. THF (anhydrous, 100 ppm BHT; Aldrich) was used without further purification or was distilled from sodium–benzophenone.

4-(4-Acetoxybutoxy)butyl acetate (1a).^[9] Procedure A: In a 50 mL 3-neck RB flask equipped with two stoppers and take-off, ytterbium triflate hydrate (1.98 g, 3.2 mmol) was charged in the flask and the reaction vessel was heated in an oil bath (125-130°C) under vacuum (0.1 mm) for 25 min. The oil bath and reaction vessel were allowed to cool to 75°C. One stopper on the reaction vessel was replaced with a thermometer adapter and thermometer, and the take-off was replaced with a Claisen head fitted with a septum and take-off. Acetic anhydride (7.5 mL, 8.1 g, 79 mmol) was added to the catalyst and stirred for 5 min. Tetrahydrofuran (15.0 mL, 13.3 g, 184 mmol) was added by syringe pump at the following rate: 5 mL at 0.8 mL/min, 5 mL at 0.6 mL/min, and 5 mL at 0.4 mL/min. At this rate of addition, the temperature of the reaction mixture remained at 77-80°C. The reaction mixture was stirred for 10 min more after the completion of the THF addition. Na4EDTA hydrate (1.23 g, 3.2 mmol) was added to the reaction mixture at 75-80°C, and, after replacement of the Claisen head with a short path distillation apparatus and the thermometer with a stopper, the reaction mixture was distilled under vacuum (2.0 mm) by heating the flask with an oil bath (100 \rightarrow 200°C). The crude distillate (b.p. 75–150°C) was redistilled under vacuum (2.0 mm) to give a forerunner containing a mixture of **1a** and **2a** (b.p. 85–130°C) and a second fraction of >98% pure 1a (b.p. 138-150°C; 12.8 g, 65% yield) as an oil. IR (film): 1739 cm^{-1} ; ¹H NMR (CDCl₃): δ 4.05 (t, 4H, J = 6.4 Hz), 3.40 (t, 4H, J = 6.2 Hz), 2.02 (s, 6H), 1.66 (m, 4H), 1.61 (m, 4H); ¹³C NMR (CDCl₃) δ 171.1, 70.2, 64.2, 26.1, 25.4, 20.9.

Procedure B: In a 25-mL Schlenk flask, ytterbium triflate hydrate (1.98 g, 3.2 mmol) was heated in an oil bath ($125-130^{\circ}$ C) under vacuum (0.1 mm) for 25 min. The oil bath and reaction vessel were allowed to cool to 75°C. Acetic anhydride (7.5 mL, 8.1 g, 79 mmol) and then tetrahydrofuran (15.0 mL, 16.9 g, 224 mmol) were added and heated in an oil bath to 75–80°C for 1 hr. Na₄EDTA (1.23 g, 3.2 mmol) was added to the reaction mixture and the reaction mixture was distilled under vacuum (2.0 mm) by heating the flask with an oil bath (100 \rightarrow 200°C). The crude distillate (b.p. 75–150°C) was redistilled under vacuum (1.0 mm) to give >98% pure **1a** (69% yield).

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4-(4-Propanoylbutoxy)butyl propanoate (1b). Using the procedure described in Procedure B for the synthesis of **1a**, **1b** (59% yield) was isolated as an oil. B.p. (1.5 mm): 155–165°C; IR (film): 1737 cm⁻¹; ¹H NMR (CDCl₃): δ 4.05 (t, 4H, J = 6.4 Hz), 3.38 (t, 4H, J = 6.2 Hz), 2.28 (q, 4H, J = 7.6 Hz), 1.65 (m, 4H), 1.61 (m, 4H), 1.09 (t, 6H, J = 7.7 Hz); ¹³C NMR (CDCl₃) δ 174.5, 70.2, 64.0, 27.5, 26.2, 25.5, 9.1.

4-[4-(2-Chloroacetyloxy)butoxy]butyl 2-chloroacetate (1c). Procedure A for the synthesis of **1a** was followed up to the distillation step of reaction mixture. The crude product was transferred to a separatory funnel with ethyl acetate (100 mL), washed with water (2 × 100 mL), 5% NaOH (100 mL), and brine (100 mL), and then dried over Na₂SO₄. (The formation of emulsions was a problem in the aqueous work-up of all reactions, so additional brine and ethyl acetate were added as needed.) The crude product was dissolved in cyclohexane/ethyl acetate (3 : 2), filtered through a plug of silica gel, and distilled under vacuum to give **1c** (42% yield) as an oil. B.p. (0.1 mm): 175–185°C; IR (film): 1755 cm⁻¹; ¹H NMR (CDCl₃): δ 4.19 (t, 4H, J = 6.4 Hz), 4.04, (s, 4H), 3.40 (t, 4H, J = 6.2 Hz), 1.71 (m, 4H), 1.61 (m, 4H); ¹³C NMR (CDCl₃) δ 167.1, 69.9, 65.9, 40.7, 25.8, 25.2. Anal. Calcd for C₁₂H₂₀Cl₂O₅: C, 45.69; H, 6.40. Found: C, 45.46; H, 6.43.

4-(4-Phenylcarbonyloxybutoxy)butyl benzoate (1d).^[26] The procedure described for the synthesis of 1c was followed until the silica gel filtration step. Column chromatography (silica gel; 95 : 5, cyclohexane : ethyl acetate) gave 1d contaminated with monomeric 2d. Recrystallization from hexane gave pure 1d (58% yield) as a white solid. M.p.: 45–47°C; IR (film): 1709 cm⁻¹; ¹H NMR (CDCl₃): δ 8.03 (d, 4H, J = 7.3 Hz), 7.54 (t, 2H, J = 7.5 Hz), 7.42 (t, 4H, J = 7.7 Hz), 4.34 (t, 4H, J = 6.4 Hz), 3.48 (t, 4H, J = 6.4 Hz), 1.85 (m, 4H), 1.74 (m, 4H); ¹³C NMR (CDCl₃) δ 166.6, 132.8, 130.4, 129.5, 128.3, 70.3, 64.7, 26.3, 25.6.

4-[4-(2-But-2-enoyloxy)butoxy)butyl]butyl but-2-enoate (1e). Using similar conditions as described for the synthesis of 1c, 1e (56% yield; E:Z, 96:4) was isolated by distillation as an oil. B.p. (0.1 mm): 158–165°C; IR (film): 1722, 1659 cm⁻¹; ¹H NMR (CDCl₃): δ 6.91 (dq, 2H, J = 15.4, 7.0 Hz), 5.79 (d, 2H, J = 15.8 Hz), 4.09 (t, 4H, J = 6.4 Hz), 3.38 (t, 4H, J = 6.2 Hz), 1.82 (dd, 6H, J = 6.8, 1.8 Hz), 1.67 (m, 4H), 1.60 (m, 4H); ¹³C NMR (CDCl₃) δ 166.5, 144.4, 122.6, 70.2, 63.8, 26.2, 25.5, 17.8. Anal. Calcd for C₁₆H₂₆O₅: C, 64.41; H, 8.78. Found: C, 64.70; H, 9.15.

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1880

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