

Solid acid catalysis of tandem isomerization-lactonization of olefinic acids

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Abstract

The conversion of unsaturated acids to γ -lactones is catalyzed by the solid sulfonic acid catalysts Amberlyst-15 and Nafion SAC-13 in refluxing chlorobenzene. For 3- and 4-enoic acids, in which double bond migration is not required for γ -lactone formation, yields are 95–100%. For 5-, 6-, 9-, and 10-enoic acids, the lactone yield decreases from 95% to 25% as the distance between the olefin and carboxylic acid groups increases. Amberlyst-15 is the preferred catalyst in these reactions because of its lower cost and reusability.

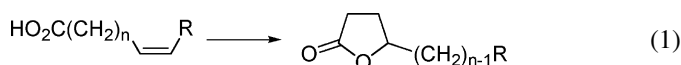
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1. Introduction

Lactones are found in the aromas of more than 120 foodstuffs and are often used as flavors and food additives [1]. The lactonization of unsaturated acids (Eq. (1)) is promoted by electrophilic reagents such as iodine, phenylselenium chloride, and mercuric and palladium salts [2–10], as well as protic acids. Fittig and Linstead reported sulfuric acid-catalyzed conversions of alk-3- and -4-enoic acids to the corresponding 5-membered-ring γ -lactones in high yields [11]. The lactonization of alk-3-enoic acids is also catalyzed by *p*-toluenesulfonic acid or phosphoric acid with a catalytic amount of perchloric acid [12]. For the lactonization of alk-3- and -4-enoic acids, cyclization can occur with no C=C bond migration. Palmer restudied these reactions and extended the substrates to C₅–C₈ alkenoic acids with the C=C bond in the 2-, 3-, 4-, 5-, or 6-position [13]. In refluxing sulfuric and trifluoroacetic acids, γ -lactones were obtained in high yields [13]. Tiecco et al. [14] and Coulombel and Duñach [15] used trifluoromethanesulfonic acid to catalyze lactonization of various substituted alk-3- and -4-enoic acids to afford γ -lactones in good yield. For long chain unsaturated

acids, such as oleic acid, with the double bond at the 9-position, sulfuric acid gave poor yields [16]. Noble prepared γ -stearolactone in 91% yield from oleic acid by using a stoichiometric amount of 70% perchloric acid in place of sulfuric acid [17].



Replacement of conventional, toxic and polluting Bronsted and Lewis acid catalysts with eco-friendly reusable solid acid heterogeneous catalysts such as acidic zeolites, clays, sulfated zirconia and ion exchange resins is an area of current interest [18]. The use of solid acid catalysts instead of liquids has advantages such as ease of product separation, recycling of the catalyst, reduced equipment corrosion, and environmental compatibility. Amberlyst-15 resin, a sulfonated polystyrene, and Nafion, a perfluorinated sulfonic acid resin, have been used as solid acid catalysts in a wide variety of reactions [19,20]. Amberlyst-15 has been used for the catalytic lactonization of 3-nonenic acid in an undergraduate laboratory experiment [21]. The Nafion resin/silica composite catalyst (Nafion SAC-13) has a larger surface area, and it shows significantly improved catalytic activity over the gel-type Nafion resin beads [19,22]. In the present study, the lactonization of unsaturated acids was carried out with the following catalysts: Amberlyst-15 resin, a gel-type Nafion resin NR-50, and a Nafion resin/silica

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Table 1
Physical properties of solid acid catalysts

Catalyst	Surface area (m ² /g)	Acid capacity (meq.H ⁺ /g)	Hammett acidity function (<i>H</i> ₀)
Amberlyst-15	0.35	4.8	−2.2
Nafion NR-50	0.02	0.89	−12
Nafion SAC-13	200	0.12	−11 to −13

nanocomposite SAC-13. Some of the properties of these acid catalysts are summarized in Table 1 [19,23].

2. Experimental

2.1. General methods

Amberlyst-15, Nafion SAC-13 and Nafion NR-50 were purchased from Aldrich. All other reagents and solvents were of A.C.S. certified grade or higher and were used as received from commercial suppliers. Routine ¹H and ¹³C NMR spectra were recorded on Varian VXR-400 or Bruker DRX-400 spectrometers. Mass spectra were measured on a Finnigan TSQ 700 spectrometer. HRMS were recorded on a Kratos MS 50 mass spectrometer. Capillary gas chromatography was performed on a HP-6890 instrument equipped with a flame ionization detector (GC column: DB-5 column, length 30 m, diameter 0.25 mm, film thickness 0.25 μm). GC–MS analyses were performed on a Finnigan TSQ 700 or Magnum ITD instrument.

2.2. General procedure for the solid acid-catalyzed lactonization reactions

A mixture of the unsaturated acid (1.0 mmol) and solid acid (usually 92 mg) in the appropriate solvent (5.0 mL) was stirred at reflux under N₂. For kinetic studies, the solid acid was added after the solution reached reflux to fix the start of the reaction. The progress of the reaction was monitored by GC and, if necessary, GC–MS. Products of these reactions were identified by comparison of their mass spectra and GC retention times with those of authentic samples. After the reaction reached completion, the catalyst was separated by filtration and washed with CH₂Cl₂. The original filtrate and CH₂Cl₂ washings were combined and solvents were removed under reduced pressure to provide pure product (**1b–3b**). Dodecane was used as the internal standard in the reactions of **1a–4a**, and hexadecane was used as the internal standard in the reactions of **5a** and **6a** in order to determine product yields. Authentic samples of **1b**, **2b**, **4b**, **4c** and **5b** were purchased from Aldrich, and **6b** was synthesized by the Nafion SAC-13 catalyzed lactonization of neat oleic acid **6a**.

2.2.1. (1b)

Using the general procedure, 6-heptenoic acid **1a** (147 mg, 1.1 mmol) and Nafion SAC-13 (101 mg) produced **1b** as a clear oil in 95% GC yield and 82% isolated yield. ¹H NMR (400 MHz, CDCl₃, δ): 4.52–4.43 (m, 1H, CH-O), 2.5 (dd, 2H,

J = 9.4 Hz, 7.0 Hz, α-CH₂), 2.35–2.23 (m, 1H, β-CH₂), 1.90–1.77 (m, 1H, β-CH₂), 1.77–1.65 (m, 1H, δ-CH₂), 1.61–1.50 (m, 1H, δ-CH₂), 1.50–1.40 (m, 2H, ε-CH₂), 0.94 (t, 3H, *J* = 7.4 Hz, CH₃) ppm. These data matched those recorded from authentic samples. ¹³C NMR (75 MHz, CDCl₃, δ): 14.1 (CH₃), 18.8 (ε-CH₂), 28.3 (δ-CH₂), 29.1 (β-CH₂), 37.9 (α-CH₂), 81.1 (CH-O), 177.6 (C=O). EIMS *m/z*: M⁺ 128.

2.2.2. (2b)

Substrate **2a** was converted by all three solid acid catalysts to **2b** in 100% GC yield and 75% isolated yield as a clear oil. ¹H NMR (400 MHz, CDCl₃, δ): 4.62 (tt, 1H, *J* = 7.6, 6.4 Hz, CH-O), 2.56–2.48 (m, 2H, α-CH₂), 2.38–2.28 (m, 1H, β-CH₂), 1.86–1.74 (1H, m, β-CH₂), 1.38 (d, 3H, *J* = 6.4 Hz, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, δ): 21.2 (CH₃), 29.3 (β-CH₂), 29.8 (α-CH₂), 77.5 (CH-O), 177.6 (C=O). EIMS *m/z*: M⁺ 100.

2.2.3. (4b)

cis-5-Dodecenoic acid **4a** (198 mg, 1.0 mmol) was converted to **4b** using the general procedure with Nafion SAC-13. ¹H NMR spectroscopy indicated that the crude product included γ-dodecalactone **4b**, represented by a diagnostic methine proton resonance at 4.45 ppm, and unidentifiable by-products. No olefinic groups were observed in the ¹H and ¹³C NMR spectra. The GC yield of **4b** was 64%. EIMS *m/z* for crude mixture: [M + 1]⁺ 199 (**4b**), [M + 1]⁺ 201 (saturated monomeric acid isomer by-products), [M]⁺ 396 (dimer by-products). The crude product was dissolved in 60 mL of CH₂Cl₂ and the resulting solution was extracted with aqueous NaHCO₃ (3 × 30 mL). Then, the CH₂Cl₂ layer was washed with brine and dried over Na₂SO₄. Removal of the solvent under reduced pressure and purification of the residue by flash chromatography (3 × 35 cm silica gel, eluent: hexane/ethyl acetate 10:1) provided 109 mg (55%) of **4b** as a clear oil from the first fraction. The remaining eluent contained several inseparable components as determined by TLC. ¹H NMR of **4b** (400 MHz, CDCl₃, δ): 4.45 (tt, 1H, *J* = 7.4, 6.4 Hz, CH-O), 2.54 (dd, 2H, *J* = 9.6, 9.2 Hz, α-CH₂), 2.35–2.23 (m, 1H, β-CH₂), 1.90–1.76 (m, 1H, β-CH₂), 1.75–1.65 (m, 1H, δ-CH₂), 1.65–1.50 (m, 1H, δ-CH₂), 1.50–1.15 (m, 12H, 6CH₂), 0.85 (t, 3H, *J* = 6.8 Hz, CH₃). These NMR data are the same as those recorded from an authentic sample of **4b**. ¹³C NMR (75 MHz, CDCl₃, δ): 14.0 (CH₃), 22.6 (CH₂), 25.2 (CH₂), 28.0 (CH₂), 28.8 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 31.8 (β-CH₂), 35.5 (CH₂–C=O), 81.0 (CH-O), 177.2 (C=O). EIMS *m/z*: M⁺ 198. The combined aqueous NaHCO₃ extract was neutralized with 6N HCl at 0 °C and then extracted with ethyl acetate (3 × 30 mL). The combined ethyl acetate layers were washed with brine and dried over Na₂SO₄. Removal of the solvent under reduced pressure afforded 28 mg of a complex mixture of saturated monomer acid isomers (C₁₂H₂₄O₂) that could not be separated by chromatography. ¹H NMR of acid residues (400 MHz, CDCl₃, δ): 2.33 (broad triplet, 2H), 1.61 (br, 3H), 1.50–1.10 (br, 9H), 0.84 (broad triplet, 3H). ¹³C NMR (75 MHz, CDCl₃, δ): 180.0 (C=O). Other carbon atoms are observed as multiple peaks in the range of 10–40 ppm. EIMS *m/z*: [M + 1]⁺ 201.

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