Article
Substrate-Dependent Selectivity in Sc(OTf)₃-Catalyzed Cyclization of Alkenoic Acids and N-Protected Alkenamides

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Abstract: Five- and six-membered ring lactones and lactams are ubiquitous frameworks in various natural and synthetic molecules and are key building blocks in organic synthesis. Catalytic addition of an O-H or N-H bond across an unactivated C–C double bond is an appealing approach to rapidly access such highly valuable N- and O-containing skeletons in a waste-free and 100% atom efficient process. Herein, we report, for the first time, the efficient and high-yield cyclization of δ/ε-alkenoic acids and N-protected δ-alkenamides catalyzed by practical and easily accessible Lewis acid scandium(III) triflate under thermal and microwave conditions. The selectivity outcome of the reaction of δ/ε-alkenoic acids was dependent on the substitution patterns of the backbone chain and alkene moiety, leading to the exclusive formation of either the corresponding γ-/δ-lactones via an O-selective cyclization or the Friedel–Crafts-type product by C-selective cyclization. An uncommon and rarely disclosed O-selective cyclization occurred preferentially or exclusively when N-protected δ-alkenamides were engaged in the reaction. The atom selectivity of the cyclization was unambiguously confirmed by single crystal X-ray crystallography.

Keywords: alkene hydrofunctionalization; scandium triflate; lactones; lactames; Friedel–Crafts; alkenoic acids; alkenamides

1. Introduction

Five- and six-membered ring lactone and lactam skeletons are undoubtedly some of the most common and recurrent structural heterocyclic motifs found in the naturally occurring and synthetic molecules covering a wide spectrum of biological activities [1–3]. Such structural moieties are also important building blocks in organic synthesis. Therefore, it is not very astonishing that the development of synthetic routes to access such prevalent N- and O-containing scaffolds has attracted the all-embracing attention of the scientific community leading to a rich arsenal of diverse (bio)chemical methodologies via distinct synthetic approaches [4–13]. Among them, the catalytic addition of an O–H or N–H bond across an unactivated C–C double bond is an appealing approach to access γ- and δ-lactones or -lactames in a waste-free, 100% atom efficient process from easily accessible alkenoic acids or alkenamides. Surprisingly, in contrast to the tremendous research activity on related processes from alkenols and alkenamines and their fruitful achievements [14–16], only few catalytic systems have been developed so far [17–31]. Moreover, most of these systems featuring a Brønsted or Lewis acid and/or an early or late transition metal as the main catalyst components and are relatively restricted in term of scope and structural diversity (Figure 1a). Therefore, there is still a need for catalyst development to propose a truly efficient O–H and N–H bond addition methodology on alkenes to access key five- and six-membered ring lactones and lactams.
Over the years, rare-earth triflates encompassing Sc(OTf)₃, Y(OTf)₃ and Ln(OTf)₃ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have emerged as privileged Lewis acid catalysts to promote a wide range of challenging chemical organic transformations [32–36]. These triflate salts feature an environmentally benign character, moderate cost and availability and retain their catalytic activity in the presence of a broad array of Lewis bases, thus exhibiting outstanding functional group tolerance. Among them, Sc(OTf)₃ has attracted particular attention due to its additional advantages comprising high Lewis acidity, stability even towards hydrolysis (water-compatibility), remarkable catalytic activity and recycling ability [37–39]. With regard to these appealing features, it is surprising that rare-earth triflates and in particular Sc(OTf)₃ have never been investigated as sustainable catalysts to access γ/δ-lactone or -lactam scaffolds from alkenoic acids or alkenamides by hydrofunctionalization. Herein, we report our endeavors to the development of such methodology. For the first time, we have efficiently catalyzed the cyclization of δ/ε-alkenoic acids and δ-alkenamides in high-to-moderate yields under thermal and microwave conditions using easily accessible and practical scandium(III) triflate (Figure 1b). The selectivity outcome of the reaction was dependent on the substituent pattern of the backbone chain and alkene moiety. For δ/ε-alkenoic acids, the corresponding lactone or Friedel–Crafts product were formed either when a rare O-cyclization occurred preferentially or exclusively when N-protected δ-alkenamides were engaged in the reaction.

2. Results

We initially investigated the cyclization of pent-4-enoic acid 1a catalyzed by common rare-earth triflates as a model reaction to afford γ-methyl-γ-butyrolactone 2a. Screening experiments led to an optimized set of reaction conditions employing Sc(OTf)₃ (10 mol%) as the catalyst in toluene at 110 °C for 16 h. These conditions regioselectively and exclusively gave 2a with 99% yield. Figure 2 summarizes the influence of some parameters that govern the reaction outcome. First, the choice of the rare-earth triflate salt influenced the reaction efficiency. Moderate-to-poor yields were obtained when Sc triflate was replaced by anhydrous Y, La, Yb or aqua Yb salt (Figure 2a). It was also found that the temperature altered the reaction yield, with 90% obtained at 100 °C while only 53% was obtained at 80 °C (Figure 2b). Moreover, no cyclization was noticed at 40 °C. Regarding the nature

(a) Previous works on γ/δ-lactones and -lactames formation by catalytic alkene hydrofunctionalization

(b) This work: Sc(OTf)₃-promoted cyclization of δ/ε-alkenoic acids or N-protected δ-alkenamides

Figure 1. (a) Previous works on γ/δ-lactones and -lactames formation by catalytic alkene hydrofunctionalization and (b) this work.
of the solvent, unsurprisingly, the use of coordinating solvent as THF or water did not lead to any significant activity (<5% yield) likely for catalyst inhibition (Figure 2c). DCE also failed to afford a satisfying yield. Decreasing the catalyst loading to 5 mol% still provided 2a in high yield in contrast to 1 mol%, for which only a 19% yield was observed (Figure 2d). Analogue optimization studies conducted on δ-alkenoic acids 1b featuring a dimethyl-induced Thorpe–Ingold effect led to the same set of optimal reaction conditions (Table S1).

![Figure 2](image_url)

**Figure 2.** Optimization studies for rare-earth triflate-catalyzed γ-methyl-γ-butyrolactone formation by alkene hydrofunctionalization. *a* yields were determined by 1H NMR using 1,3,5-trimethoxybenzene as the internal standard.

With these optimized set of reaction conditions in hand for the formation of 2a, the cyclization of various δ-alkenoic acids featuring different substitution patterns on the alkyl chain and the alkene moiety was examined. To our surprise, the reaction outcome was highly dependent on these patterns, which led either to the expected lactone compounds by O-selective cyclization (Figure 3) or the Friedel–Crafts products by C-selective cyclization (Figure 4). As expected from the cyclization of 1a, δ-alkenoic acids 1b–f bearing a monosubstituted olefin that have a Thorpe–Ingold effect are suitable substrates for this Sc(OTf)3-catalyzed cyclization. Indeed, under our optimized cyclization conditions, 1b–f afforded the corresponding γ-methyl-γ-butyrolactone products 2b–f in excellent NMR yields and good isolated yields when the backbone is disubstituted by either a methyl (2b), cyclohexyl (2c), phenyl (2d), 4-t-Butylcyclohexyl (2e) group or the combination of a methyl and a phenyl (2f) (Figure 3). Likewise, 2-Vinyl benzoic acid (1g) can also be converted into 3-methylisobenzofuran-1(3H)-one (2g) in 89% isolated yield. The 6-membered ring δ-methyl δ-valerolactone 2h could also be formed in 99% NMR yield from the corresponding ε-alkenoic acid 1h under our conditions. To our satisfaction, our methodology is also appropriate for the cyclization of δ-alkenoic acids featuring more challenging di- and trisubstituted alkenes as exemplified by the reactivity of 1i and 1j, which afford 2i and 3j in 74% and 79% yield, respectively. As expected, in contrast to 2a–h, the formation of 3j proceeds by an *endo*-cyclization. Surprisingly, under our conditions, the cyclization of 1l with a phenylvinyl substituent led to a complex mixture of undefined products.

In contrast to 1a–j, when the backbone of the δ-alkenoic acids bears electron-rich phenyl groups at the geminal position and at a potential stabilized cation at the terminal position (via a phenyl or two methyl substituents) of the alkene, our Sc(OTf)3-catalyzed protocol did not provide the expected lactone but led exclusively to cyclization via C-C bond formation between one of the phenyl backbone substituents and the more stabilized carbon of the alkene, similar to a Friedel–Crafts reaction; the acid functionality was left intact. Indeed, heating 1m at 80 °C in toluene for 16 h led exclusively to the formation of a Friedel–Crafts product 4m in 99% NMR yield (91% isolated yield) with no trace of...
O-selective cyclization product (Figure 4). The structure and relative configurations of 4m were unambiguously confirmed by X-ray analysis of a single-crystal (Figure 5). This singular C–C bond formation was not restricted to 1m because other δ-alkenoic acids featuring R1 substituent on the backbone aromatic groups distinct from H evolved through a similar reactivity pattern under these conditions. Cyclization of 1n and 1o having a t-Bu or a MeO group at R1 solely gave the Friedel–Crafts product 4n and 4o in 98% and 95% isolated yields, respectively. Changing the R2 and R3 substituents of the C–C double bond to methyl did not alter the reaction selectivity and efficiency because compound 4p was isolated in a high yield. It is interesting to note that this cyclization protocol does not require the presence of the acid functionality because it could be transposed to alkenoic ester 1q without losing efficiency. However, no reaction was noticed with alkenoic acids 1r and 1s bearing a phenyl and chloro substituent, respectively, at R1 position, which reflects the electronic sensitivity of the reaction. To our knowledge, such divergent reactivity has not been reported in the context of alkene hydrofunctionalization of alkenoic acids, thus highlighting the peculiar ability and richness of scandium triflate to bring structural diversity in the alkene hydrofunctionalization field.

Figure 3. Formation of γ- and δ-lactones by Sc(OTf)3-catalyzed cyclization of alkenoic acids featuring mono-, di- and trisubstituted olefins. c a yields were determined by 1H NMR using 1,3,5-trimethoxybenzene as the internal standard; b isolated yields; c all reactions run under thermal conditions unless otherwise stated; d run under microwave conditions.
After the successful selective Sc(OTf)₃-catalyzed cyclization of δ-alkenoic acids, the application scope of our rare-earth-catalyzed methodology was extended to N-protected δ-alkenamides (Figure 6). To our delight, when N-tosyl alkenamide 5a featuring a gem-dimethyl group was subjected to reaction under the optimized conditions developed for δ-alkenoic acids, quantitative conversion was observed. Unexpectedly, O-selective cyclization occurred preferentially to N-selective cyclization leading to the formation of N-product 6a and O-product 7a in a 1:2.4 ratio which could be isolated in 28% and 61% yields, respectively. The structural assignments for both isomers were unambiguously confirmed by X-ray diffraction analyses of a single-crystal (Figure 7). ¹H and ¹³C NMR spectra and IR spectroscopy. In the ¹³C and ¹H NMR spectra, the chemical shifts of the tertiary carbon and its related proton are distinctive between the N- and O-cyclized product (δC = 179.0 ppm and δH = 4.30 ppm for 6a; δC = 179.9 ppm and δH = 4.76 ppm for 7a). Moreover, IR data are characteristic of both isomers (νC=O = 1726 cm⁻¹ for 6a; νC=N = 1618 cm⁻¹ for 7a) and are consistent with data reported in the literature for related classes of compounds [40,41]. Such divergences from N- to O-selective cyclization leading to O-cyclized products preferentially
are well-known in halocyclization of ambident nucleophiles (such as urea, carbamate or amide) tethered to alkenes, and elegant methodologies to circumvent such regiocontrol switch have been reported [42–47]. mCPBA-mediated cyclization of N-tosyl δ-alkenamides also produce mostly O-cyclized products by an oxyhydroxylation reaction [48]. However, such O-preferential regioselectivity in the field of alken monofunctionalization are rarely described. Indeed, most of the sporadic examples of cyclization of N-protected δ-alkenamides state N-selective bond formation [28–30,49–51] and, to our knowledge, only two reports disclosed O-cyclization from ambident alkenamides by efficient cobalt-hydride-promoted processes [41,52]. This scarcity underscores the potential of using scandium triflate to introduce molecular diversity and to access versatile but less-studied functional groups as cyclic N-sulfonyl imidates [53]. Our Sc(OTf)3-catalyzed methodology was also efficient for the selective cyclization of a range of N-protected δ-alkenamides. Replacing the gem-dimethyl substituents by a cyclohexyl did not change the ratio of N-/O-cyclized product (Figure 6). To our delight, the cyclization of N-tosyl alkenamide 5c featuring a gem-diphenyl group afforded O-selective product 7c in 79% isolated yield and in a satisfying N-/O-selectivity ratio of 1:12. The structure of 7c was unambiguously confirmed by X-ray diffraction analysis of a single-crystal (Figure 7). Introducing bulkier 4-t-ButC6H4- groups at the geminal position of the substrate backbone also allowed us to isolate the corresponding 7e product in 75% yield (1.9 ratio). In contrast, N-tosyl alkenamide 5d was unbiased toward cyclization by the chain substituents, which led to a slight preference (6d/7d = 1.4:1) for the N-cyclization as noticed by 1H NMR. Next, we examined the influence of the protecting-group R2 of 5 on the cyclization selectivity and found that our methodology is not restricted to the tosyl-protecting group because Ms-, PhSO2- or 4-MeOC6H4- are also compatible. Indeed, high yields of O-cyclized products 7f, 7g or 7h are obtained with exclusive or high O-selectivity. However, the cyclization of alkenamide 5 featuring an R2 substituent equal to H (5i), Bn (5j) or Tf (5k) are beyond the reach of the present Sc(OTf)3-based system.

![Figure 6](image_url)

**Figure 6.** Sc(OTf)3-catalyzed cyclization of N-protected δ-alkenamides. *a* isolated yields; *b* ratio of N-selective product vs. O-selective product determined by 1H NMR on the crude reaction mixture; *c* all reactions run under thermal conditions unless otherwise stated; *d* run under microwave conditions.
Microwave-assisted organic synthesis is nowadays an important and essential tool for medicinal chemists to develop efficient syntheses toward N-containing heterocycles because it has proven various benefits including a reduction of reaction time, an increase in product yield, and purity in an environmentally friendly manner in comparison to conventional thermal methods [54,55]. To exploit these benefits, we conducted the Sc(OTf)3-catalyzed cyclization of δ-alkenoic acids of 1b and 1d (Figure 3), 1m (Figure 4) and δ-alkenamide 5c (Figure 6) as model substrates under microwave conditions. Gratifyingly, in all cases, the reaction time could be drastically reduced without any loss of selectivity or efficiency. Indeed, under microwave conditions, the reaction of 1b, 1d and 5c led to complete conversion into O-selective cyclized products 2b, 2d and 7c in 1h, 1h and 10 min, respectively, thus giving isolated yields similar to those obtained under thermal conditions (Figures 3 and 6). A 10 min-reaction time also allows the full conversion of 1m into the Friedel–Crafts product 4m as a sole product (Figure 4). These results underline the strong beneficial effect in term of reaction time of conducting this Sc(OTf)3-catalyzed methodology under microwave conditions.

3. Materials and Methods
3.1. Materials and Instrumentation

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl. Toluene and diisopropylamine were distilled over CaH2. n-BuLi (2.5 M in hexanes) was purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France) and was used as received. Scandium (III) trifluoromethanesulfonate (Sc(OTf)3) was purchased from TCI and was used as received. Silica gel (Merck, type 60, 0.04–0.063 mm) was used for column chromatography. Pent-4-enoic acid (1a) and 2-vinylbenzoic acid (1g) were purchased from Sigma Aldrich company, and 1-cyclopenten-1-ylacetic acid (1j) was purchased from BLD Pharmatech Ltd (Shanghai, China). 1H and 13C NMR data were recorded on Bruker 400, Bruker 360, Bruker 300 or Bruker 250 spectrometers at 22 °C. Chemical shifts were reported as the δ unit with reference to the residual solvent resonance. Mass spectra were recorded on MicrOTOFq Bruker spectrometer by electrospray ionization. Melting points were determined using a Reichert melting point apparatus. Infrared spectra were recorded on a FTIR spectrometer (Bruker Vertex 70 ATR Pike Germanium) and only major peaks were reported in cm⁻¹. Microwave experiments were conducted using a CEM Discover Synthesis Unit (monomode system) operating at 2450 MHz monitored by a PC computer. X-ray diffraction data were collected at 200 K by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) (see Supplementary Materials for details).
3.2. Experimental Methods

3.2.1. General Procedure for the Sc(OTf)₃-Catalyzed Cyclization of Alkenoic Acids and Alkenamides under Thermal Conditions

The appropriate alkenoic acid 1a–1s or alkenamide 5a–5k (0.23 mmol, 1 equiv) and Sc(OTf)₃ (11.6 mg, 0.023 mmol, 10 mol%) were charged in a screw-cap vial equipped with a stir bar. Toluene (1 mL) was added, and the tube was sealed. The reaction mixture was stirred at 110 °C for 16 h. Then, toluene was removed under vacuum and the crude product was purified by flash column chromatography on silica gel using different gradients of petroleum ether and acetone (and 1% acetic acid for 1m–p).

3.2.2. General Procedure for the Sc(OTf)₃-Catalyzed Cyclization of Alkenoic Acids or Alkenamide 5c under Microwave Conditions

Alkenoic acids 1b or 1d or 1m or alkenamide 5c (0.23 mmol, 1 equiv), Sc(OTf)₃ (11.6 mg, 0.023 mmol, 10 mol%) and toluene (1 mL) were added in a 5 mL microwave vial before the tube was sealed with a vessel cap. Then, the reaction tube was left for 1 h (1b or 1d) or 10 min (1m or 5c) under microwave with a 300 W power. Toluene was then removed under vacuum and the crude product was purified by flash column chromatography on silica gel using different gradients of petroleum ether and acetone (and 1% acetic acid for 1m).

4. Conclusions

In conclusion, we have herein explored the Sc(OTf)₃-catalyzed cyclization of δ/ε-alkenoic acids and N-protected δ-alkenamides under thermal and microwave conditions for the first time. Under both reaction conditions, the selectivity outcome of the transformation of δ/ε-alkenoic acids was directly correlated to the substitution patterns on the alkyl backbone chain and the alkene moiety. When the backbone of the δ/ε-alkenoic acids bears electron-rich phenyl groups at the geminal position and a potential stabilized cation at the terminal position of the alkene, exclusive high-yield formation of the corresponding Friedel–Crafts-type product by C-selective cyclization between a backbone phenyl group and the olefin occurred. In contrast, other studied substitution patterns led to the sole formation of the corresponding γ/δ-lactone via an O-selective cyclization in high yields. The lactone formation methodology was compatible with alkenoic acids featuring mono-, di- and trisubstituted alkenes. Under thermal or microwave conditions, the Sc(OTf)₃-catalyzed hydrofunctionalization reaction of N-protected δ-alkenamides proceeded via an original and rarely reported O-selective cyclization either preferentially or completely. This work highlights the great potential of using a simple Lewis acid as scandium triflate to unravel original and unprecedented reactivities and introduce molecular diversity. Further investigations in this direction are underway in our laboratory.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12111481/s1, Synthesis and spectral data of δ/ε-alkenoic acids and N-protected δ-alkenamides, spectral data and copies of ¹H and ¹³C NMR spectra for cyclized products. References [1–19] are cited in the Supplementary Materials.

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