DOI: 10.1002/ejoc.201001201

Macrocyclisation of Macrodiolide with Dimethylaluminium Methaneselenolate

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Keywords: Macrocyclization / Macrodiolides / Aluminum / Selenium / Pyrenophorin

Dimethylaluminium methaneselenolate ($Me_2AlSeMe$, **1**) acts as an acyl transfer agent for esterification. In cases of direct macrolactonisation (n = 10–12), this selenium–aluminium complex preferentially creates symmetric macrodiolides rather than macrolides. The factors determining macrodilactonisation were investigated and applied toward the total synthesis of norpyrenophorin, which result in a macrodilactonisation yield of 64 %.

Introduction

A selenium–aluminium compound, dimethylaluminium methaneselenolate (**1**), was first synthesised in 1960[1] and later used as an acyl transfer reagent.[2,3] Although selenium can form a moderately stable complex with aluminium,[4,5] few reports in the literature have described the function of dialkylaluminium selenolate in organic syntheses.[2] Kozikowski and Ames[2,3] developed **1** as a reactant for the production of various methyl selenol esters. Compound **1** exhibits features of both organoaluminium and organoselenium compounds. Although it was derived from a "hard" Lewis acid, the acidity of **1** is sharply decreased by the replacement of a methyl group with a methaneselenol anion. In addition, **1** rarely participates in anionic methylation because of the diminished mobility of the methyl group as observed with aluminium alkoxide or aluminium alkylthiolate.[6,7]

Similarly to other organoselenium compounds, the "soft" base nature of selenium lengthens the covalent bond between selenium and aluminium to approximately 2.34–2.38 Å.[4,8] This lengthening generally facilitates the construction of a new C–Se bond,[2,3,6] especially in the formation of selenol esters.[2,3,9] The lability of selenol esters depends on the nucleophilicity of the carbonyl group and the mobility of the $MeSe^-$ anion.[9,10] Therefore, a selenol ester accompanied by a strong nucleophile, such as a hydroxy group, is an interesting intermediate that can convert into corresponding carbonyl compounds by intra- or intermolecular routes. In addition, because selenium and aluminium atoms also have a relatively high oxygenophilicity, complex formation can occur with **1** and ω-hydroxy ester compounds, in which the neutral aluminium(III) and selenium species attract the neutral base, carbonyl or hydroxy group, and each species can react with the other through stepwise or concerted routes. Under such conditions, the acylation of hydroxy groups may be accelerated such that bimolecular esterification proceeds to completion before both ends of the single molecule have an opportunity to encounter three or more other molecules, which would be required to form linear of cyclical structures. Therefore, the current study focuses on one-pot macrodilactonisation reactions with **1**.

Naturally occurring macrodiolides, isolated and assessed over the past few decades, have not only demonstrated enormous potential as antibiotics and antitumour therapeutics but also compounds such as **2**, **3** and **4** have served as synthetic targets.[11–13] Many macrolactonisation methods have been established and are currently used in organic synthesis (Figure 1).[11–15] Although a mixture is generally obtained, concentrated solutions yield cyclic macrodiolide dimers in greater proportions than their monomeric counterparts. A novel, one-pot macrodilactonisation reaction is described herein by using compound **1** without further activation of the carbonyl group and irrespective of concentration. Macrolide formation was not detected during this reaction.

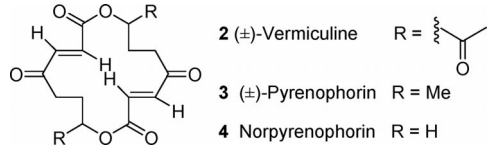

Figure 1. Various macrodiolides.

Results and Discussion

As noted by Kozikowski and Ames,[2,3] nucleophilic attack at the carbonyl of the selenol ester, and consequent

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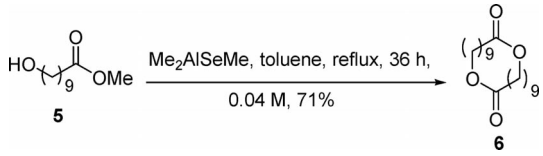
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001201.

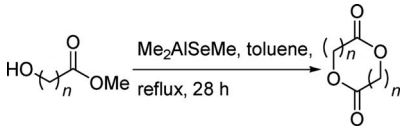
leaving of the alkyl selenol, results in the formation of other carbonyls, such as esters, amides or ketones, through two or more intermolecular steps. Upon heating, a solution of ω-hydroxy methyl ester and **1** results initially in a new selenol ester. The hydroxy group then acts as a nucleophile, and together with the aluminium and carbonyl group, quickly forms an ester.

Although classic macrolactonisation methods can be applied in macrodilactonisation reactions, the current study explores the various differences between techniques. A ω-hydroxymethyl ester (**5**) was chosen as a model and heated at reflux in toluene with **1**. As expected, the 22-membered ring macrodiolide (**6**) was obtained in 71% yield without a trace of monomeric macrolide (Scheme 1). Upon encountering **1**, the flexible methylene chain of the ω-hydroxymethyl ester rotates significantly. Under such harsh conditions, classic esterification methods would likely have resulted in macrolide (monomer lactone) generation. However, the macrodiolide (dilactone) compound obtained was much larger than a monomer. Two factors influence the relative yields of mono- and dilactones: the concentration of material and the interaction rate between the methyl ester and the selenium–aluminium complex. With regard to the former, the data in Table 1 show that the influence of concentration on the relative yield of the dimer and monomer is insignificant. Investigation of the latter was not performed here.



Scheme 1. One-pot macrodilactonisation.

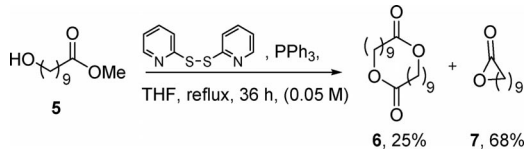
Table 1. Macrodilactonisation with dimethylaluminium methaneselenolate ($Me_2AlSeMe$, **1**).



Entry	*n*	[Starting material] [mmol/mL]	Isolated yield [%]	
			Dimer	Monomer
1	9	0.01	63	A
2	10	0.1	68	<10
3	10	0.04	71	<10
4	10	0.005	48	13
5	11	0.02	61	[a]

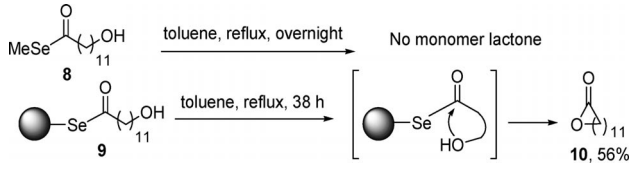
[a] Not detected.

Comparisons were also made with classic lactonisation directed by a thiolester intermediate. As predicted on the basis of general principles,[12] the monolactone was obtained in high yield, accompanied by a 25% yield of the dilactone, from a moderately concentrated solution of ω-hydroxymethylester treated with dipyridyl disulfide (Scheme 2). This result contrasts sharply with earlier observations. As shown in Scheme 1, the formation of dilactone is favoured over the formation of monomer or oligomers. The interaction probability of reactants increases with increasing concentration to produce more polymeric products in both open and closed conformations. By these standards, the current results are unconventional and lead to the conclusion that the selenol ester intermediate, which was rapidly generated and consumed, is less stable than the corresponding thiolester. Ester formation proceeded so rapidly that the aluminium-coordinated hydroxy group had no chance of encountering an intramolecular methyl ester group. In other words, in a moderately concentrated solution, if two molecules were to interact with each other under the direction of **1**, their termini will form a new ester bond in a very short time.



Scheme 2. Macrolactonisation with dipyridyl disulfide.

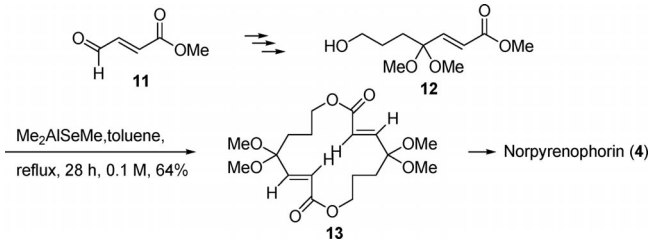
Table 1 shows the absence of a correlation between the carbon chain length and the relative yields of monomer and dimer. The ω-hydroxyselenol ester was separated and heated at reflux overnight in toluene; no monomer lactone or diolides were produced (Scheme 3). However, when the selenol ester was fixed to a solid support, the terminal neutral base was able to access the carbonyl group as a result of carbon chain flex during reflux. This scenario is illustrated in Scheme 3, which shows the selenol ester linked to a Tentagel resin. The selenol-linked resin was heated at reflux in toluene for 38 h to obtain the macrolide (monolactone) in majority yield.



Scheme 3. The solid-phase reaction of a ω-hydroxyselenol ester.

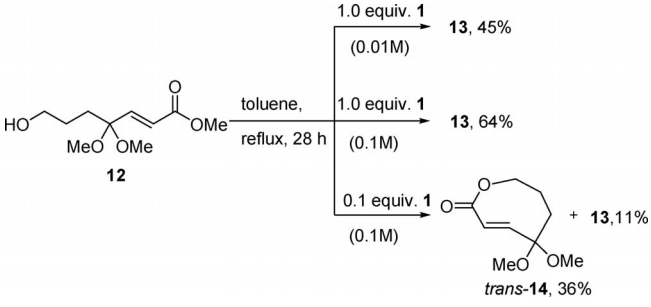
The above phenomenon demonstrates the violent movement of the ω-hydroxyselenol ester in refluxing toluene. However, the esterification is still an energy-intensive process. Although the alkyl selenyl anion[16] is a good leaving group, it is not sufficient to activate inter- or intramolecular esterification. The results are quite different in the presence of aluminium. Compound **1** likely plays a significant role in the dilactonisation process by coordinating the hydroxy group and triggering selenol ester formation. This would then induce the alkyl oxide transformation to the corresponding ester as in Scheme 6.

To demonstrate the synthetic utility of this process, a novel one-pot macrodiolisation was performed for the total synthesis of norpyrenophorin (Scheme 4).



Scheme 4. Total synthesis of norpyrenophorin.

Compound **12** was treated with 0.1 M and 0.01 M of **1** in toluene to obtain norpyrenophorine in high yield. In the former case, norpyrenophorine was obtained in 64% yield, but the latter concentration yielded only 45%. The rigid fan shape of compound **12**, and its ketal group, permits a greater degree of contact with other molecules, including **1**. By heating **12** at reflux with catalytic amounts of **1** (0.1 equiv.), *trans*-α,β-unsaturated monolactone (**14**) was formed, as shown in Scheme 5. A comparison of molecular energies of the *trans*-(**14**) and *cis*-α,β-unsaturated monolactone **15**, shown in Figure 2, reveals that the *trans* conformation is more sterically rigid than the *cis* conformation. The *trans* precursor will therefore be less likely to form monocyclic structures. Nevertheless, when catalysed with **1**, a twisted monolactone was created from the *trans*-α,β-unsaturated ω-hydroxy ester **12**. This implies the recycling of compound **1** as a result of direct esterification. More precisely, the oxygen neutral base, which was coordinated with aluminium(III) through the carbonyl group of the selenol ester, will form the new ester bond, while the resulting methyl selenyl anion will complex with aluminium to recover the initial compound **1** and result in the lactone molecule shown in Scheme 6.



Scheme 5. Macrodilactonisation and macrolactonisation by using dimethylaluminium methaneselenolate ($Me_2AlSeMe$, **1**).

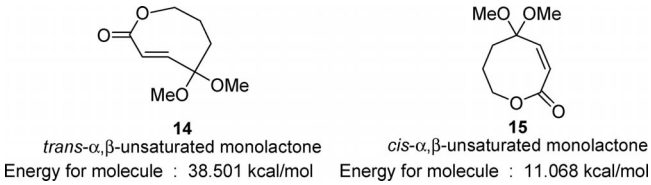
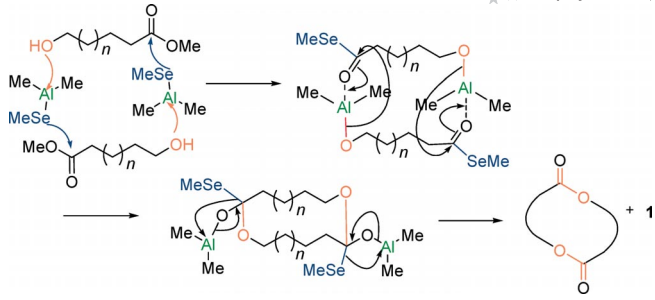


Figure 2. *cis*- and *trans* isomers of macrolides.



Scheme 6. Possible mechanism of macrodilactonisation with dimethylaluminium methaneselenolate ($Me_2AlSeMe$, **1**).

Conclusions

Direct macrodilactonisation with the selenium–aluminium complex, dimethylaluminium methaneselenolate (**1**), was observed for the first time. This selenium–aluminium complex generally participates in selenol ester formation and exhibits characteristics of both a "hard" Lewis acid and a "soft" Lewis base. When complex **1** was treated with methyl ω-hyroxyl ester, a single macrodiolide was preferentially formed through the interaction of two identical ω-hydroxy esters. Although the selenol ester was formed initially, the acyl transfer agent was insufficient for intramolecular lactonisation. Aluminium may play an important role by coordinating with the neutral base and carbonyl and hydroxy groups (Scheme 6). By using catalytic amounts of **1** with compound **12**, the monolactone formed despite the *trans* conformation of the α,β-unsaturated ester. With this method, the full synthesis of norpyrenophorin was carried out with a total yield of 14.9%.

Experimental Section

General Procedure: All reactions were performed under a fume hood. Selenium powder was activated under vacuum at approximately 100 °C for 4–6 h. Toluene was treated with calcium hydride and distilled under argon prior to its use in the reactions. Dichloromethane was distilled by using calcium hydride, and tetrahydrofuran (THF) was distilled by using sodium metal with benzoquinone. ω-Hydroxycarboxylic acids were obtained from Sigma–Aldrich Co. and converted to methyl esters in a solution of methanol and concentrated sulfuric acid. Analytical thin-layer chromatography (TLC) was performed on commercial silica gel plates (silica gel 60 F_{254}, Merck). Flash chromatography was performed on silica gel 60 (63–200 mesh, Merck). NMR spectra were recorded on Varian Gemini (200 MHz) and Bruker (400 MHz) spectrometers. ^1H NMR spectra were obtained at 200 and 400 MHz. ^{13}C NMR spectra were obtained at 50 and 100 MHz. High-resolution mass spectra were obtained on a Micromass FAB-EI and ESI spectrometer. FTIR spectra were obtained by using a JASCO FTIR spectrometer. The resulting compounds were separated by using a fresh chromatography column prior to calculating the yield.

Macrolactonisation and Macrodilactonisation with 1,12-Dioxacyclodocosane-2,13-Dione (6) and Oxacycloundecan-2-one (7)

The Corey–Nicolaou Method:[15] 2,2′-Dipyridyl disulfide (220.3 mg, 1.0 mmol) and triphenylphosphine (393.4 mg, 1.5 mmol) were

added to a solution of 10-hydroxyundecanoic acid (188.2 mg, 1.0 mmol) in toluene, and the solution was heated at reflux for 28 h. After cooling the mixture to room temperature, the solvent was removed by evaporation, and the residue was separated on a flash chromatography column (eluent = 20:1 *n*-hexane:ethyl acetate) to yield 116 mg of **7** (68%) and 42 mg of **5** (25%).

The Current Method: Trimethylaluminium (5 mL of a 2 M solution, 10 mmol) in toluene was added to a 50-mL side-arm flask containing selenium powder (820.0 mg, 10.4 mmol). When the selenium powder had reacted completely, the resulting mixture was cooled to room temperature. An aliquot of $Me_2SeAlMe$ (0.05 mL, 1.0 mmol) was transferred by syringe to a solution containing methyl 10-hydroxyundecanoate (188.2 mg, 1.0 mmol) in toluene (10 mL) at 0 °C. After 28 h of heating at reflux, the yellow solution was warmed to room temperature over a period of 30 min and treated with sodium sulfate. The solution was then diluted with dichloromethane, washed with water six times and treated with sodium hydrogen carbonate. The solution was then dried with brine and anhydrous magnesium sulfate. The solvent was removed under vacuum from the yellow solution, and the residue was separated by using a flash chromatography column with the same eluent as above to yield 124 mg of **5** (71%). FTIR (KBr): $\tilde{\nu}$ = 1728.87 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (br. m, 12 H, 6CH_2), 1.61 (m, 4 H, 2CH_2), 2.32 (t, J = 6.8 Hz, 2 H, CH_2), 4.11 (t, J = 5.6 Hz, 2 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.52 (*C*H_2), 26.18 (*C*H_2), 28.76 (*C*H_2), 29.08 (*C*H_2), 29.23 (*C*H_2), 29.55 (*C*H_2), 29.82 (*C*H_2), 34.99 (*C*H_2), 64.14 (*C*H_2), 174.05 (*C*H_2) ppm. ESI-MS: calcd. 340.26; found 340.91.

Norpyrenophorin (4): An aliquot of $Me_2SeAlMe$ (0.1 mL, 2.0 mmol) was transferred by syringe to a solution containing **12** (436.5 mg, 2.0 mmol) in toluene (10 mL) at 0 °C. After heating at reflux for 28 h, the yellow solution was warmed to room temperature over a period of 30 min and treated with moist sodium sulfate. The solution was then diluted with dichloromethane, washed six times with water and treated with sodium hydrogen carbonate. The solution was then dried with brine and anhydrous magnesium sulfate. The solvent was removed from the yellow solution by vacuum evaporation, and the residue was separated by using a flash chromatography column (eluent = 5:1 *n*-hexane/ethyl acetate) to yield **13** as a colourless liquid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.57 (m, J = 5.0 Hz, 4 H, 2CH_2), 3.18 (s, 3 H, CH_3), 4.16 (t, J = 5.0 Hz, 2 H, CH_2), 6.12 (d, J = 16.0 Hz, 1 H, C*H*), 6.57 (d, J = 16.0 Hz, 1 H, C*H*) ppm.

The colourless liquid was dissolved in a 3:1:1 solution of AcOH/H_2O/THF, heated at reflux for 1 h, quenched with sodium hydrogen carbonate and diluted with dichloromethane. The solution was washed three times and treated with brine, dried with $MgSO_4$, filtered and concentrated to obtain a colourless liquid. After purification by silica gel chromatography (eluent = 1:1 *n*-haxane:ethyl acetate), 151 mg of white powder was obtained with 54% yield over two steps. FTIR (KBr): $\tilde{\nu}$ = 1731.76, 1645.95 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.37 (m, J = 7.16 Hz, 2 H, CH_2), 2.84 (t, J = 6.96 Hz, 2 H, CH_2), 4.30 (t, J = 7.12 Hz, 2 H, CH_2), 6.67 (d, J = 16.2 Hz, 1 H, C*H*), 7.02 (d, J = 16.2 Hz, 1 H, C*H*) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.70 (*C*H_2), 36.89 (*C*H_2), 53.42 (*C*H_2), 128.86 (*C*H), 139.89 (*C*H) ppm. EI-MS: calcd. for $[M + H]^+$ 281.09; found 281.12.

Supporting Information (see footnote on the first page of this article): ^1H NMR, ^{13}C NMR, IR and mass spectra of the solid-phase reaction and the synthesis of norpyrenophorin are presented.

Acknowledgments

This work was supported by a Korea Research Foundation grant funded by the Korean government (MOEHRD; KRF-2005-041-E00499) and the Seoul R&BD Programme (10524). We thank Prof. Park Hyun-ju (College of Pharmacy, Sungkyunkwan University) for calculating the molecular energies of compounds **13** and **14**.

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Received: August 25, 2010
Published Online: November 12, 2010

