Preparation of *E*- and *Z*-α-Arylidene-γ-butyrolactones from *Z*-α-Stannylmethylene-γ-butyrolactones: Stereoselective Synthesis of (±)-Savinin and (±)-Gadain

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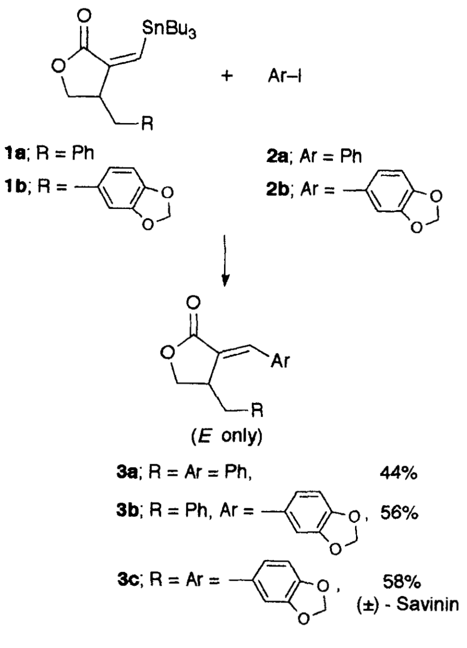
E-α-Arylidene-γ-butyrolactones were prepared by the radical addition–elimination reaction of *Z*-α-stannylmethylene-γ-butyrolactones, whereas the palladium(0) catalysed cross-coupling reaction of the same substrates afforded *Z*-α-arylidene-γ-butyrolactones.

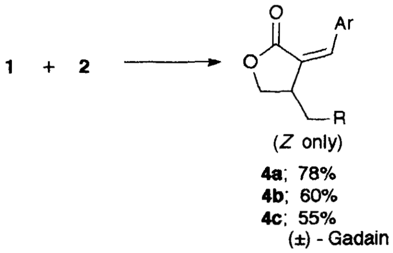
Recently we reported a convenient method for the synthesis of *Z*-α-stannylmethylene-γ-butyrolactones which were easily transformed into α-methylene-γ-butyrolactones upon destannylation.[1] Vinylstannanes may serve as substrates in more useful transformations.[2–4] We now report substitution reactions of *Z*-α-stannylmethylene-γ-butyrolactones with aryl halides which result in the formation of α-arylidene-γ-butyrolactones. Two methods were considered for the elaboration of a stannylmethylene group into an arylidene group: aryl radical addition–stannyl radical elimination and palladium-catalysed cross-coupling reaction with aryl halides. The chemistry of α-stannylmethylenelactones is not well known yet, and the above reactions may lead to alternative synthesis of lignan lactones.[5]

The *Z*-α-stannylmethylene-γ-butyrolactone **1** substrates were prepared from appropriate allylic propiolates in 60–80% yields by slow addition of tributylstannane solution containing 0.15 equiv. of azoisobutyronitrile (AIBN).[1] A solution of **1** (2.0 mmol) and the aryl halide **2** (1.0 mmol) in benzene (3.0 ml) was heated under reflux and a solution of tributylstannane (1.0 mmol) and AIBN (0.1 mmol) in benzene (3.0 ml) was added by a syringe pump over 5 h. Products were isolated in 44–58% yields along with recovered substrates.[6] *E*-α-Arylidene products **3** were obtained exclusively. 3,4-Methylenedioxyphenyl iodide **2b** participated in the substitution reaction, thus paving the way for the synthesis of (±)-savinin **3c**.[6]

Z-α-Arylidene-γ-butyrolactones **4** were synthesized *via* palladium-catalysed arylation. A solution of the lactone **1a**

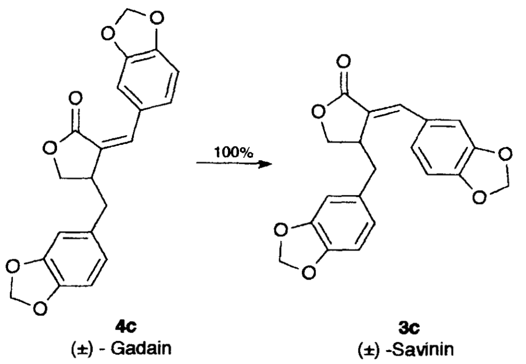


Scheme 1 *Reagents and conditions*: Bu$_3$SnH, AIBN (cat.), slow addition (5 h), refluxing C$_6$H$_6$



Scheme 2 *Reagents and conditions*: Pd(dba)$_2$, refluxing toluene (12 h) for **4a**; Pd(dba)$_2$, DMF (80 °C, 16 h), Bu$^n_4$NI for **4b,c**; **4a–c**, **a–c** as for **3**

(1.0 mmol), iodobenzene **2a** (1.0 mmol) and a catalytic amount of bis(dibenzylideneacetone)palladium [Pd(dba)$_2$; 5 mol%] in toluene (3.0 ml) was heated under reflux to give *Z*-α-benzylidene-β-benzyl-γ-butyrolactone **4a** in 78% yield. 3,4-Methylenedioxyphenyl iodide **2b** did not participate in the palladium(0)-catalysed substitution reaction in toluene, but in dimethylformamide (DMF) with a phase-transfer catalyst the reaction proceeded in reasonable yield.[7] (±)-Gadain **4c** was synthesized in this way in 55% yield.[8] The *Z*-α-arylidene-γ-butyrolactones **4** were quantitatively isomerised into the corresponding *E*-isomers **3** under the radical generating conditions. For example, the treatment of (±)-gadain **4c** (1.0 mmol) with tributylstannane (1.0 mmol) in the presence of a catalytic amount of AIBN in boiling benzene (3.0 ml) for 1 h gave (±)-savinin **3c** quantitatively.†



Scheme 3 *Reagents and conditions*: Bu$_3$SnH, AIBN (cat.), refluxing C$_6$H$_6$, 1 h

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† In ^{1}H NMR spectra, the vinylic hydrogen resonances of the *Z*-α-arylidene-γ-butyrolactones always appear downfield relative to the corresponding signal in the *E*-isomers: for example, δ 7.72 for gadain and δ 7.50 for savinin.