

A DIRECT SYNTHESIS OF (\pm)-ELDANOLIDE VIA THE HIGHLY REGIOSELECTIVE PRENYLATION OF
2-TRIMETHYLSILOXYFURAN¹

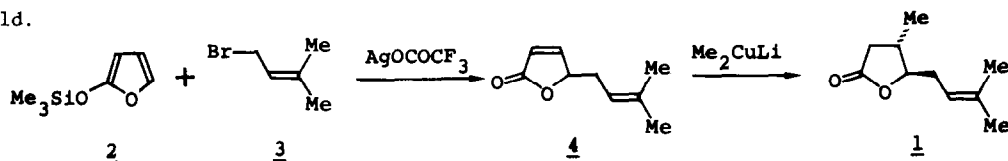
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Summary. The reaction of 2-trimethylsiloxyfuran, 3,3-dimethylallyl bromide and silver trifluoroacetate produced (3,3-dimethylallyl)-4-but-2-en-4-olide with high double regiodifferentiation. The latter compound on treatment with lithium dimethylcuprate gave (\pm)-eldanolide in high yield.

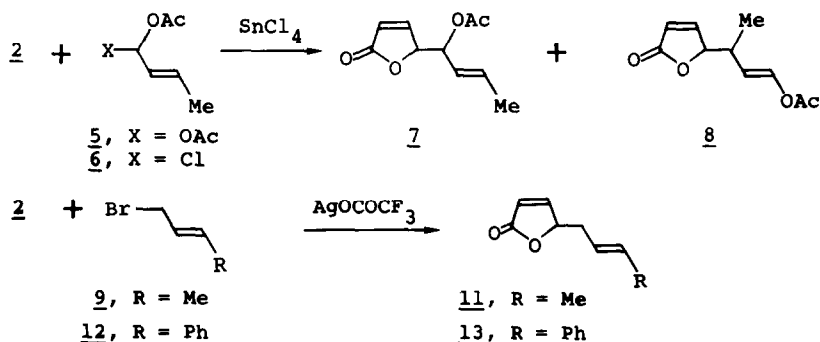
Eldanolide (1) is the sex attractant pheromone of the male African sugar cane borer *Eldana saccharina* (Wlk).² The borer can severely damage sugar cane and maize crops.³ Therefore, its control is an agronomic necessity. A possible method would be to use synthetic pheromone as bait combined with a suitable insecticide.⁴ Notwithstanding the many syntheses of 1 reported so far,^{5,6} there is still a need for a simple gram-scale preparation. We now describe a short route to (\pm)-1 which demonstrates the potential of the commercially available 2-trimethylsiloxyfuran (2) as a keystone in γ -lactone synthesis.⁷

Our strategy was to effect the regiocontrolled prenylation of 2 to create the relay butenolide 4, which could then be converted to 1 in just one additional step.⁸ This plan was realized as follows. A solution of 2 (1 eq) and 3,3-dimethylallyl bromide⁷ (3, 1.05 eq) was treated with silver trifluoroacetate (1.05 eq) in dry dichloromethane under argon at -78° for 20 min. The resulting mixture was allowed to warm to -20° over 3 h. After 10 min at 24°, aqueous work-up gave butenolide 4 in 95% yield. The absence of isomeric products shows that only the desired bond was formed. This means that the reaction between 2 and 3 is doubly regioselective as coupling occurs exclusively between the C4 and C1 atoms respectively.⁹ The subsequent treatment of 4 with lithium dimethylcuprate furnished racemic 1 in 78% overall yield.



Although the prenylation of silyl enol ethers has received much attention,¹⁰ less is known about the alkylation of 2 or silyl 1,3-dienol ethers with potentially ambident halides.¹¹ The choice of catalyst is certainly critical. If zinc bromide was used, 2 and 3 afforded a complex mixture containing 30% of 4 at the most. Earlier it was reported that 2 on reaction with 1,1-diacetoxybut-2-ene (5) or its 1-chloro analogue 6 when catalyzed with tin tetrachloride gave a mixture of the regio-isomers 7 and 8 in a 1:1 ratio¹². In contrast, an equilibrium mixture¹³ of crotyl (9) and α -methylallyl bromides (10) (87:13) produced a single product 11 in quantitative yield from 2 and silver trifluoroacetate. Trans cinnamyl bromide (12) behaved similarly, giving 12.¹⁴

The high regioselectivity and reactivity of **2** as has been shown above, make it an eminently suitable reagent for constructing, simply and efficiently, naturally occurring γ -lactones. Further examples will be reported elsewhere.



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7. 2-Trimethylsiloxyfuran and 3,3-dimethylallyl bromide are sold by Fluka, CH-9470 Buchs, Switzerland.
8. Racemic butenolide **4** has been previously obtained in 5 and 7 steps (refs. 5a, 5c) and then transformed to (\pm)-**1**.
9. NMR (360 MHz) examination of the reaction mixture revealed no isomers of **4**.
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14. Compounds **11** and **14** gave compatible analytical and spectral data.

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