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EFFICIENT TRANSFORMATION OF (Z)-2-BUTENE-1,4-DIOLS TO α,β-BUTENOLIDES: A SIMPLE SYNTHESIS OF (±)-ELDANOLIDE

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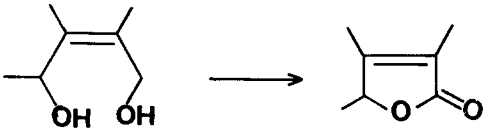
Abstract. (Z)-2-Butene-1,4-diols are efficiently converted to the corresponding α,β-butenolides using silver carbonate/celite and this methodology has been applied to the synthesis of (±)-eldanolide, the wing gland pheromone of the male African sugar cane borer, *Eldana saccharina* (wlk)

There are a large number of methods available in the literature for the synthesis of butenolides[1-5] and in recent years there has been a renewed interest in the synthesis of structurally simple α,β-butenolides.[6] In connection with our studies on oxidation with pentavalent chromium reagents[7] we were interested in an efficient transformation of (Z)-2-butene-1,4-diols to α,β-butenolides.



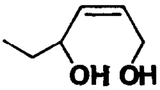
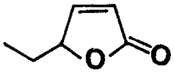
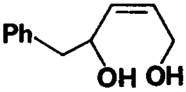
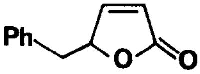
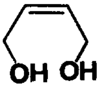
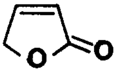
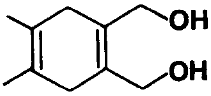
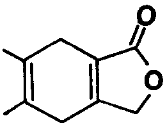
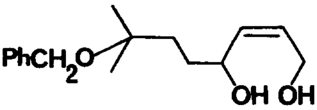
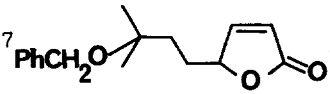
In a recent report Itoh *et al.*[8] observed that a number of (Z)-2-butene-1,4-diols on oxidation with a variety of chromium and manganese derived oxidising agents were smoothly converted to the corresponding substituted furans in good yields rather than to the α,β-butenolides. This transformation was believed to take place *via* a one step oxidation-dehydration process. Independently White[9] published his observation on a similar transformation. Oxidation with $RuH_2(PPh_3)_4$ on the other hand resulted in lactonization along with hydrogenation of the carbon-carbon double bond.[10]

Herein, we wish to describe the first successful, general method for the oxidation of (Z)-2-butene-1,4-diols to substituted α,β-butenolides with silver carbonate/celite[11-13] and its application to the synthesis of (±)-eldanolide, the wing gland pheromone of the male African sugar cane borer, *Eldana saccharina* (wlk).[14-17]

Treatment of (Z)-2-butene-1,4-diols 1a-1e with six equivalents of silver-carbonate/celite in refluxing benzene afforded substituted α,β-butenolides 2a-2e in very good yield. The results of these oxidations are summarized in

Table.[18] This oxidation of (Z)-2-butene-1,4-diols with Fetizon's reagent suggests that the reaction conditions being neutral and mild the intermediate hemiacetals undergo further oxidation to α,β-butenolides rather than undergoing dehydration to give furan derivatives. In a typical case, a mixture of diol 1a (0.232 g, 2 mmol) and silver-carbonate/celite (6.912 g, 12 mmol) in benzene (25 ml) was refluxed for 3 h, filtered and the filtrate on concentration and purification by silica gel column chromatography gave 2a (0.18 g, 80%). The application of this method was exemplified in a short synthesis of (±)-eldanolide 5 (SCHEME-1).[19]

TABLE Oxidation of (Z)-2-butene-1,4-diols to α,β-butenolides with silver carbonate/celite[a]

Entry	(Z)-2-Butene-1,4-diol[b] 1		Reaction Time (hr)	α,β-Butenolide 2		Yield[c] (%)
1.		1a	3		2a	80
2.		1b	3		2b	56[d]
3.		1c	2		2c	78
4.		1d	8		2d	84
5.		1e	[7]		2e	75

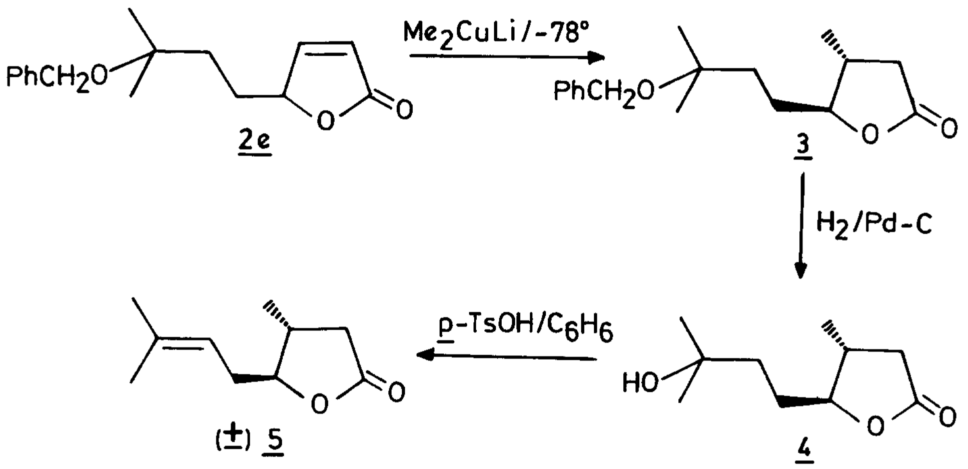
a) All reactions were carried out using six equivalents of silver carbonate/celite in boiling benzene.

b) (Z)-2-Butene-1,4-diols were prepared according to literature procedures.[8]

c) Yields refer to isolated products.

d) Some furan derivative was also isolated in this reaction.

SCHEME-1



Stereospecific conjugate addition of lithium dimethylcuprate[16,17] to 2e yielded the lactone 3 (70%). Reductive cleavage of the benzyl ether followed by dehydration with p-toluenesulfonic acid in refluxing benzene yielded (±)-eldanolide 5 (80%).[20]

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18. All new compounds gave satisfactory elemental analysis and spectroscopic data.
19. The starting material 1e was obtained from allyldimethylcarbinol in five steps in 72% overall yield: (i) $PhCH_2Cl$, NaH; (ii) B_2H_6/H_2O_2, NaOH; (iii) PCC; (iv) $THPOCH_2C{\equiv}CMgBr$; (v) p-TsOH, CH_3OH/H_2, Pd(O)-$CaCO_3$, quinoline (one-pot).
20. Eldanolide 5 gave satisfactory spectroscopic data: IR (CCl_4), 1780 cm^{-1}; ^1H NMR ($CDCl_3$), δ1.15 (d, 3H, J =7 Hz), 1.66 (s, 3H), 1.75 (s, 3H), 2.0-2.9 (m, 5H), 4.05 (q, 1H, J =6 Hz), 5.18 (br t, 1H); MS (m/e), 168 (M^+), 99, 71, 69, 43, 41.

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