

REGIOSELECTIVE FUNCTIONALISATION OF THE  $\Delta^{\alpha,\beta}$ -BUTENOLIDE RING VIA GROUP  
IV-B ORGANOMETALLICS

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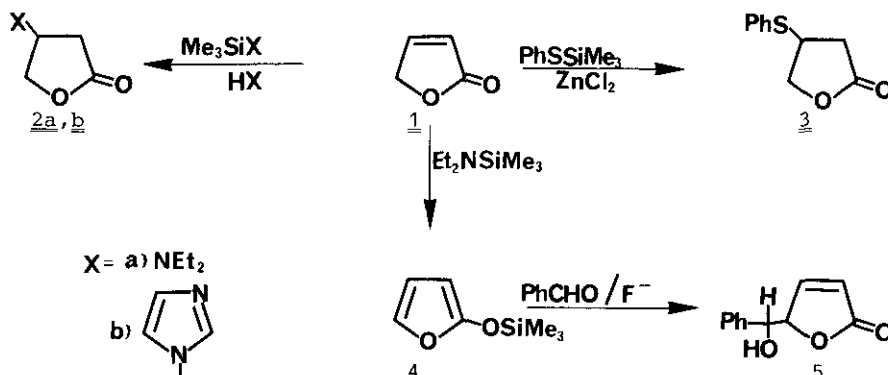
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**Abstract** - The  $\Delta^{\alpha,\beta}$ -butenolide ring reacts with amino- and thiosilanes to give 4-substituted  $\gamma$ -butyrolactone and siloxyfuran. The latter under-  
goes regiospecific functionalisation at the 5 position with benzaldehyde  
under  $F^-$  catalysis.

Although the use of  $\Delta^{\alpha,\beta}$  and  $\Delta^{\beta,\gamma}$ -butenolides as useful synthetic units is well docu-  
mented<sup>1,2</sup>, their regioselective functionalisation has been the subject of a relatively  
small number of investigations<sup>3</sup>.

We wish to report herein on a simple and general method through the reaction of  
a  $\Delta^{\alpha,\beta}$ -butenolide with an organosilane, which can be directed towards 1,4 addition  
with formation of 4-substituted  $\gamma$ -butyrolactones, or regioselective substitution  
with electrophiles at the 5 position.

Our synthetic approach is shown in the Scheme. We found that by treating buten-  
olide 1 with N,N-diethylaminotrimethylsilane in  $Et_2O$  as solvent, trimethylsiloxyfuran 4  
4 can be obtained as the main product (80% yield) along with a small amount of 2a  
from addition at positions 3 and 4. The initial addition of an equimolar amount of



diethylamine (DEA) , resulted in a sizeable increase of the yields of 2a (ca. 50%) and in a corresponding reduction of the amount of 4 (ca. 35%). In the same reaction with trimethylsilylimidazole, only a small amount of 2b was recovered from the reaction mixture; however again the initial addition of imidazole (1 equivalent) raised the yield of 2b to ca. 70%, whereas no siloxyfuran was detected among the reaction products. Analogously 1,4 addition was found to predominate in the spontaneous or  $\text{ZnCl}_2$  catalysed reaction of 1 with phenylthiotrimethylsilane in  $\text{CH}_2\text{Cl}_2$ : after quenching with water, 4-phenylthiobutyrolactone <sup>6</sup> 3 was isolated in 65% yield. Most likely the function of the amino- and thiosilanes is to drive the reaction in a regiospecific way, through interaction of the silicon atom with the carboxy oxygen of 1, developing a positive charge at position 4: nucleophilic substitution at this position or 4,5 elimination afford products 2, 3 or 4 respectively <sup>7</sup>.

In a typical reaction, a solution of  $\Delta^{\alpha,\beta}$ -butenolide 1 (3 g, 35.7 mmol) in  $\text{Et}_2\text{O}$  (5 ml) was added dropwise under argon to an equimolar mixture of DEA and N,N-diethylaminotrimethylsilane in dry  $\text{Et}_2\text{O}$  (7 ml). Samples were withdrawn at intervals and the progress of the conversion which was followed by glc, was judged to be complete after 10 h at room temperature. Evaporation of the crude reaction mixture followed by vacuum distillation, afforded 2a (bp  $140^\circ\text{C}/4$  mm Hg) in 50% yield;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.95 $\delta$  (t, 6H), 2.45 (m, 6H), 3.60 (m, 1H), 4.27 (m, 2H); IR  $1760\text{ cm}^{-1}$  ( $\nu\text{ C=O}$ ); MS 157 ( $\text{M}^+$ ), 140, 113, 100, 99.

Product 2b obtained from equimolar amounts of 1-trimethylsilylimidazole, imidazole and 1 , was purified by silica gel column chromatography (n-propanol:n-heptane / 4:1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 2.75 $\delta$  (m, 1H), 3.15 (m, 1H), 4.45 (m, 1H), 4.85 (m, 1H), 5.05 (m, 1H), 7.10 (s, 2H), 7.65 (s, 1H); IR  $1785\text{ cm}^{-1}$  ( $\nu\text{ C=O}$ ); MS 152 ( $\text{M}^+$ ), 94, 68, 55.

A somewhat different functionalisation of 1 , based on a silyl transfer reaction <sup>8</sup>, was achieved starting from compound 4 , that reacted as one equivalent of  $\alpha\Delta^{\alpha,\beta}$ -butenolide-5-carbanion: under the influence of a catalytic amount (10% mol) of silica-supported tetrabutylammonium fluoride <sup>9</sup>, the enol trimethylsilyl ether 4 reacted smoothly at room temperature in THF with an equimolar amount of benzaldehyde to give 5. Conversion of 4 into 5, was performed according to the following procedure: a solution of 1 g (6.4 mmol) of 4 and 0.60 g (6.4 mmol) of benzaldehyde in dry THF (2 ml), was added dropwise under argon to 0.26 g of TBAF/ $\text{SiO}_2$ . After 4 h at room temperature, the reaction mixture was quenched with water and extracted with  $\text{Et}_2\text{O}$ . The ethereal extracts were dried, the solvent was evaporated and the residual oil (0.9 g, 73%) was unambiguously identified as 5.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 4.25 $\delta$  (s, 1H), 4.90 (m, 1H), 5.01 (m, 1H), 6.02 (m, 1H), 7.25 (m, 5H); MS 190 ( $\text{M}^+$ ), 173, 146, 107, 105, 83, 77. This reaction gave negligible amounts of products arising from dimerisation, self-condensation and no evidence was found for the presence of the other regioisomer of 5.

The above work illustrates the high degree of regiospecificity and the versatility of the functionalisation of  $\Delta^{\alpha,\beta}$ -butenolides via 1-4 addition of Group IV-B

organometallics, whereas the  $F^-$  ion based reaction of 4 with electrophiles such as benzaldehyde recommends this technique as an interesting alternative to the methods reported earlier<sup>3</sup>.

Further investigations on the synthetic utility of these reactions are currently underway.

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