

Reactivity of α,β -Unsaturated Acetals with Electrophiles in the Presence of Organolithium–Potassium Reagents

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2-Propenyl- and 2-(2-methylpropenyl)-1,3-dioxane react with 2 equiv. of *sec*-butyllithium complexed with potassium *tert*-butoxide in tetrahydrofuran (THF) at $-95\text{ }^\circ\text{C}$ undergoing a 1,4 eliminative ring fission with subsequent proton abstraction at the α vinyl site of the enol ethers produced; carbanions obtained undergo substitution and addition reactions with electrophiles.

Depending upon structure and reaction conditions, α,β -unsaturated acetals and ketals react with organolithium reagents in pentane by addition, substitution, or proton abstraction.¹ Treatment of 2-vinyl-1,3-dioxane with butyllithium in diethyl ether or pentane has been reported to induce nucleophilic addition of RLi to the carbon–carbon double bond with concomitant cleavage of the ring carbon–oxygen bond.² A

deprotonation pathway at the α site has been reported for acrolein acetal with *sec*-butyllithium at $-95\text{ }^\circ\text{C}$.³

Because of our current interest in the reactivity of hetero-substituted allyl anions⁴ and protected carbonyl groups⁵ we report herein our results in studies on the reaction of metallated 2-propenyl- **1** and 2-(2-methylpropenyl)-1,3-dioxane **2** with electrophiles. The reactions have been carried out in the presence of 2 equiv. of *sec*-butyllithium complexed with potassium *tert*-butoxide in THF at $-95\text{ }^\circ\text{C}$,⁶ according to Scheme 1. Potassium *tert*-butoxide was added at room temperature to 10 ml of anhydrous THF. The solution was then cooled to $-95\text{ }^\circ\text{C}$ and *sec*-butyllithium was added under vigorous stirring. After a few minutes the organic substrate (**1** or **2**) was added dropwise with a syringe. The reaction mixture

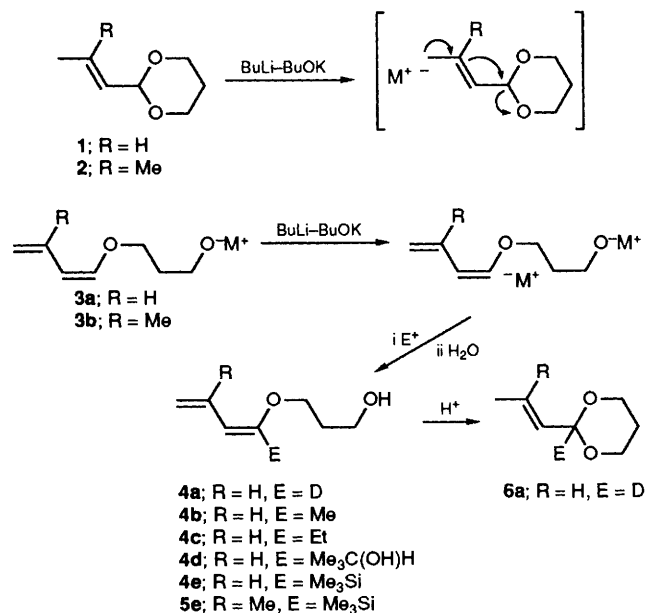


Table 1 Reaction of 2-propenyl-1,3-dioxane **1** and 2-(2-methylpropenyl)-1,3-dioxane **2** with different electrophiles, in the presence of 2 equiv. of Bu^{*t*}Li complexed with Bu^{*t*}OK^a

Electrophile	Substrate	Product	Yield ^b (%)
D ₂ O	1	4a	95
MeI	1	4b	85
EtI	1	4c	80
Me ₃ CHO	1	4d	50
Me ₃ SiCl	1	4e	90 ^c
Me ₃ SiCl	2	5e	82 ^c

^a Substrate (2.5 mmol), Bu^{*t*}Li (5.0 mmol), Bu^{*t*}OK (5.0 mmol), electrophile (2.5 mmol), THF (10 ml), $T = -95\text{ }^\circ\text{C}$. ^b Isolated yield of product purified by column chromatography, satisfactory mass spectra have been obtained for the products and their ¹H NMR spectra are in accordance with the assigned structure. ^c Working with 6.5 mmol of Me₃SiCl the *C*-, *O*-silylated product was obtained.

turns purple-red and was allowed to stand for 2 h at -95°C . After the addition of the electrophile the colour was discharged and the reaction mixture was allowed to reach -50°C , then quenched with water (2 ml) at that temperature.

As shown in Scheme 1 the reaction proceeds by: (i) proton abstraction at the unsubstituted δ site and 1,4 eliminative ring fission (**3a, b**); (ii) proton abstraction at the α terminus of the vinyl ether produced, and finally the electrophilic attack that affords the substituted enol ethers **4d, 5e**. The results obtained are reported in Table 1.

Further studies will be undertaken for converting **4** and **5** into 2,2-disubstituted-1,3-dioxanes upon treatment with a catalytic amount of acid.[†]

[†] In the case in which R = H and E = D, the enol ether spontaneously cyclizes to [2-²H]-2-propenyl-1,3-dioxane **6a**, on standing in CDCl_3 solution.

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