Facile S_N' Reaction of Alkyl-lithiums with 2-Vinyl-1,3-dioxane

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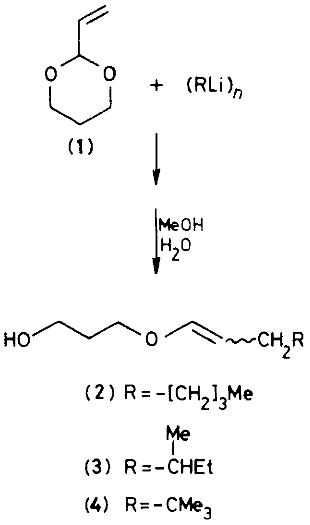
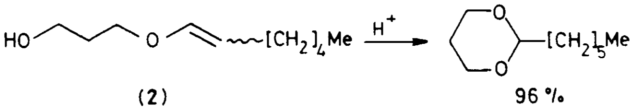
Treatment of 2-vinyl-1,3-dioxane with n-, s-, or t-butyl-lithium in diethyl ether or n-pentane solution results in facile nucleophilic addition of RLi to the carbon–carbon double bond with concomitant cleavage of the ring C–O bond (S_N' process) to give high yields of enol ethers having the structure $HO[CH_2]_3OCH{=}CHCH_2R$.

Reactivity umpolung of the classical Michael reaction is possible if the β-vinyl proton of an α,β-unsaturated acetal can be abstracted with strong base.[1] With this in mind, we have investigated the reaction of 2-vinyl-1,3-dioxane (**1**) with alkyl-lithiums. We report herein that reaction of (**1**) with n-, s-, or t-butyl-lithium (BuLi) proceeds *via* nucleophilic addition to the carbon–carbon double bond with concomitant cleavage of a ring C–O bond. This S_N' process occurs to the exclusion of proton abstraction from (**1**).



As shown in Table 1, enol ethers (**2**), (**3**), and (**4**) are produced in high yield† as *cis*-/*trans*-mixtures when either diethyl ether or n-pentane is employed as solvent. Not surprisingly, the products are extremely acid labile as demonstrated by virtually quantitative conversion of (**2**) to 2-n-hexyl-



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† Satisfactory high-resolution mass spectroscopic molecular weights have been obtained for the enol ethers and their i.r., ^1H n.m.r., and ^{13}C n.m.r. spectra are in accord with the assigned structures. The enol ethers were purified by Kugelrohr distillation at the following bath temperatures: (**2**), 72—80 °C (0.15 Torr); (**3**), 80—83 °C (0.2 Torr); (**4**), 95—96 °C (0.2 Torr).

Table 1. Reaction of alkyl-lithiums with 2-vinyl-1,3-dioxane (**1**).

Alkyl-lithium	Reaction temperature, °C	Product	Yield,[a] (*E*-/*Z*- ratio)[b] Et$_2$O solvent	Pentane solvent
Bu^{n}Li	0	(**2**)	84 (80/20)	80 (84/16)
Bu^{s}Li	−70	(**3**)	88 (90/10)	79 (90/10)
Bu^{t}Li	−70	(**4**)	80 (85/15)	80 (85/15)

[a] Isolated yield of purified product. [b] Determined by integration of the relevant signals in the ^{1}H n.m.r. spectrum of purified material: *i.e.* δ 4.8 and 6.2 (*J ca.* 12.5 Hz) for *E*-isomers; δ 4.4 and 6.0 (*J ca.* 6.4 Hz) for *Z*-isomers.

1,3-dioxane upon treatment with a catalytic quantity of acid (Amberlyst-15).

Although behaviour similar to that described herein (Table 1) has recently been observed upon attempted anionic polymerization of α,β-unsaturated acetals,[2] formal S_N' reaction of an alkyl-lithium with olefinic substrates is generally not a facile process.[3] In contrast to the high-yield S_N' reaction of RLi with (**1**) in either diethyl ether or n-pentane solvent, alkyl allyl ethers have been reported to undergo S_N' reaction with an alkyl-lithium only at elevated temperature in hydrocarbon solution.‡ The ease with which (**1**) is attacked is most likely a consequence of prior complexation between RLi and the ring-oxygens of (**1**). Such co-ordination with heteroatoms is known to activate RLi toward nucleophilic addition to alkenes.[3,5]

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‡ Treatment of alkyl allyl ethers with alkyl-lithium in hydrocarbon solution at low temperature leads to proton abstraction while in ethereal solution Wittig rearrangement is the dominant process. *Cf.* ref. 4.

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