Ring-Formation from Allyl- and Vinylstannanes Initiated by Treatment with Butyl-Lithium

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Abstract The allylstannane 1 and the vinylstannanes 3, 5 and 7 cyclise when treated with butyl-lithium.

Allyl- and vinylstannanes undergo rapid tin-lithium exchange when treated with butyl-lithium at -78 °C.¹ This reaction might be used in ring formation if the allyl- or vinylstannane has an electrophilic centre at a suitable distance, provided, of course, that the tin-lithium exchange is faster than the reaction between butyl-lithium and the electrophilic centre. Much of Piers' work has been based on avoiding this possibility, by having the electrophilic centre at an unsuitable distance from the intermediate vinyl-lithium species.² However, he has used it deliberately to form a cyclopentane, using a vinylstannane that was also a primary alkyl chloride.³ More recently, Yamamoto has achieved cyclisations by adding butyl-lithium to some allylstannanes having an epoxide group five and six atoms away from the allyl unit.⁴ Similar reactions, but with dithianylstannanes and α -alkoxystannanes rather than allyl- or vinylstannanes, have been established by Seebach,⁵ McGarvey,⁶ and Linderman,⁷ with epoxides and amides as the electrophilic groups. Chlorides, epoxides and amides are effective because they are relatively slow to react intermolecularly with butyl-lithium. Some even less electrophilic groups, like a terminal alkene⁸ and allyl ethers,⁹ have also been shown not to interfere with tin-lithium exchange, and yet permit cyclisation. In contrast, butyl-lithium attacked an ester group faster than it induced tin-lithium exchange with some α -alkoxystannanes.⁷

We wondered how far this possibility could be taken with allyl- and vinylstannanes. Could it be used with electrophilic groups like ketones? They are known to react within minutes with butyl-lithium at temperatures in the region of -70 °C,¹⁰ yet cyclisation might still occur, if the tin-lithium exchange is even faster. Alternatively, could it be used to form the less favourable ring sizes, by choosing an electrophilic group that is very resistant to attack by butyl-lithium? We now report examples of each of these possibilities, indicating that this method of making rings has greater scope than has perhaps been realised.



We^{11,12} and others¹³ have already reported that stannyl-cupration of allenes and acetylenes, followed by treatment with α,β -unsaturated ketones or ethylene oxide, can be used to set up the starting materials for the present investigation. Thus we have reported the synthesis of the the allylstannane 1¹¹ and the vinylstannanes 3,¹² from the allene or acetylene and cyclohexenone. When these compounds were treated with butyl-lithium, the major products were the cyclopentanol 2 and the cyclopentenols 4, respectively.

Similarly, we have reported^{11,12} that the stannyl-cupration of allene, acetylene and phenylacetylene, followed by treatment with ethylene oxide, give the primary alcohols from which we prepared the ptoluenesulfonates 5 and 7. When these compounds were treated with butyl-lithium, the major products were the cyclobutane 6 and the cyclobutenes 8, respectively.



The success of the reactions with the ketones is in marked contrast to the failure to achieve tin-lithium exchange in the vinylstannane 9, where the products reported by Quayle and his co-workers were the ketone 11 and the tertiary alcohol 12, which appear to have been produced, without tin-lithium exchange, by direct attack of the butyl-lithium on the ester group.¹⁴ We suggest that the success of our reactions and the failure of Quayle's might indicate that the reactive species in each case is not the product of completed tin-lithium exchange, but an intermediate pentacovalent tin anion. If the intermediate makes the allyl and vinyl units nucleophilic enough to attack the ketone, then the tin-lithium exchange may not need to be consummated before ring-formation takes place. In Quayle's case, the intermediate 10 might deliver the butyl group to the carbonyl group, by way of a five-membered ring transition state, faster than vinyl-lithium formation.



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