ALLYLSTANNANES AS ELECTROFUGAL PARTNERS IN ALLYLIC ALKYLATION
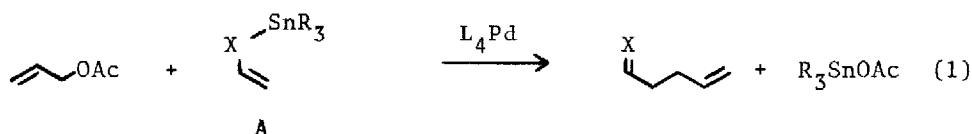
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Abstract. Unsymmetrical allyl-allyl couplings occur between allylstannanes and allyl acetates catalyzed by palladium(O) and a novel direct coupling of an allyl acetate in the presence of a distannane and a palladium(O) catalyst is also possible.

The reaction of allyl acetates with nucleophiles catalyzed by palladium has allowed a host of applications in organic synthesis[1]. Efforts to expand the scope of the reaction with respect to the nucleophilic partner has shown the value of tin chemistry[2]. Whereas, the reaction of simple enolates was unpromising, enol stannanes appear to be excellent nucleophiles (see eq. 1).

$$\text{\textasciitilde\textasciitilde OAc} \quad + \quad \underset{\mathbf{A}}{X\text{\textbackslash}SnR_3} \quad \xrightarrow{\ L_4Pd\ } \quad X\text{\textasciitilde}\text{\textasciitilde} \quad + \quad R_3SnOAc \quad (1)$$

In this communication, we wish to record that replacement of oxygen by carbon in $\mathbf{A}$ led to coupling.

Treatment of 1 eq of cinnamyl acetate with 1.4 eq of α-methallyl-tri-n-butylstannane[3] and 4 mol % of tetrakis(triphenylphosphine)palladium $\underset{\sim}{1}$ in dry THF at reflux for 6 hr led to a 69% yield of $\underset{\sim}{3}$[5]. The regio- and stereochemistry of $\underset{\sim}{3}$ is clearly established by NMR spectroscopy (for ex. δ 5.26, dt, J = 15.5, 5.5 Hz, 1H, and 6.45, d, J = 15.5 Hz, 1H). Use of tetra-allylstannane led to $\underset{\sim}{4}$ in 71% yield.

The regiochemistry with respect to the allylstannane was established with crotyl-tri-n-butylstannane[4] which gave, as the only coupling product, $\underset{\sim}{5}$ in 32% yield in addition to 1- and 3-phenylpropene (product of reduction of the allyl acetate). This regiochemistry is clearly established by NMR
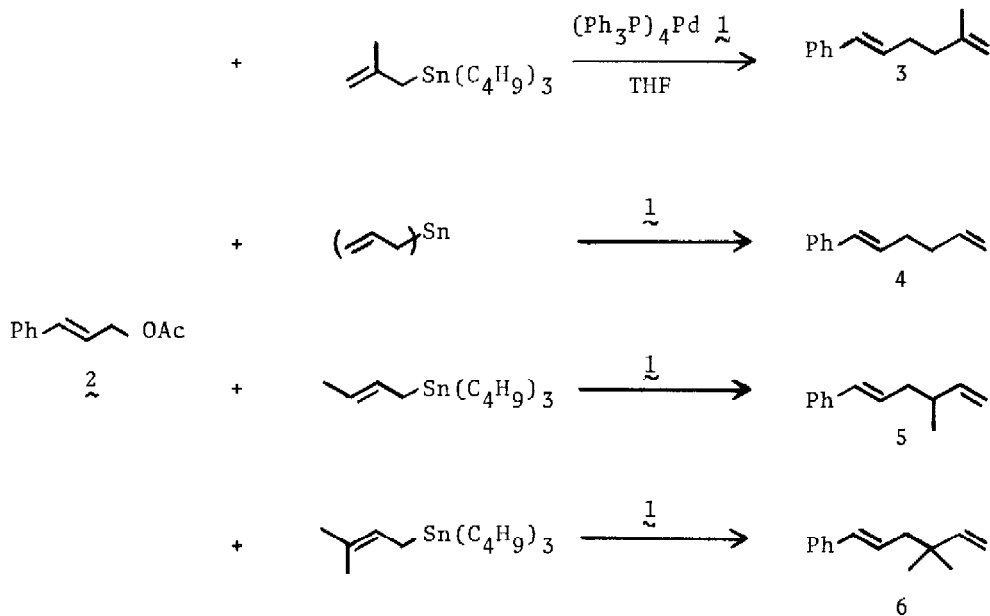
spectroscopy which shows a saturated methyl group (δ 1.04, d, J = 6 Hz), a terminal vinyl group (δ 4.98, d, J = 10.5 Hz; 5.02, d, J = 17.5 Hz;, 5.84, ddd, J = 17.5, 10.5, 6.5 Hz) and a E disubstituted double bond (δ 6.21, dt, J = 16, 6 Hz; 6.41, d, J = 16 Hz). Complete allyl inversion of the allyl-stannane was also observed for prenyl-tri-n-butylstannane to give 6; however, the steric hindrance of the tertiary center of the prenyl group led to a very low yield (4%) of coupling product.

A symmetrical coupling was also possible by treatment of 2 with hexa-n-butyldistannane in the presence of 1[6]. In this reaction, cinnamyl-tri-n-butylstannane is presumably generated in situ, catalyzed by palladium,
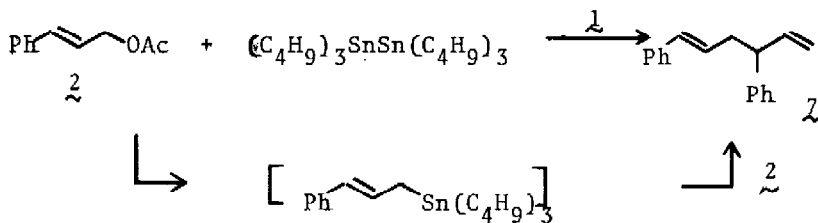
which then couples with 2 with allyl inversion of the cinnamylstannane to give 7 in 51% yield.

The selective transfer of an allyl group over an alkyl group in the mixed stannanes is not surprising from a bond energy point of view[7,8]. However, use of prenyltriphenylstannane led to 1,3-diphenylpropene[9] (19%) as the only
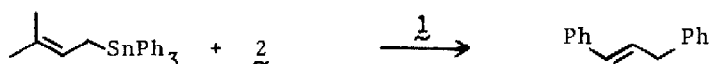

detectable coupling product. The exclusive transfer of the phenyl group contradicts bond energy arguments as a factor in the rationale of the coupling reaction.

The mechanism of this reaction can only be speculative at the present. Transfer of the R group from tin to palladium (eq 2) seems unlikely. Transfer
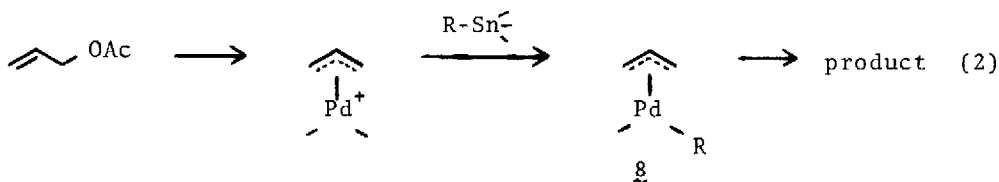
of saturated alkyl groups to Pd (+2) intermediates is known[8]. Invoking such a reaction would lead to the expectation that such groups would couple in this reaction. Use of tetra-n-butylstannane led to no coupling products. Further, invoking an intermediate such as 8 would suggest scrambling of the allyl carbons of the allylstannane which is not observed. Direct attack on a π-allylpalladium intermediate (eq 3) is a viable explanation and would rationalize the reactivity pattern and clean allyl inversion[7a,c] observed for the allylstannanes. Such a reaction was also observed for an allylsilane
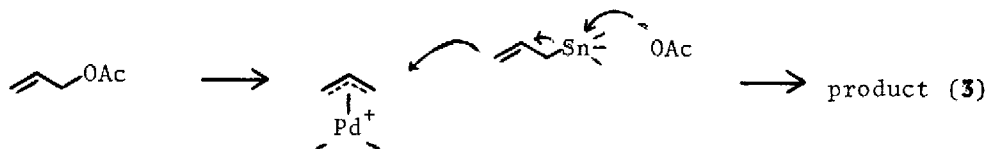
(eq 4) but was limited to 3-trimethylsilylindene[10]. In this case, the retention of configuration observed in the displacement suggests a pathway analogous to that in eq 3. Unfortunately, attempts to determine the stereochemistry of the stannane reaction in similar fashion were thwarted by the total dominance of the elimination of the elements of acetic acid from the allyl acetate[11]. However, by analogy to the allylsilane case, a similar

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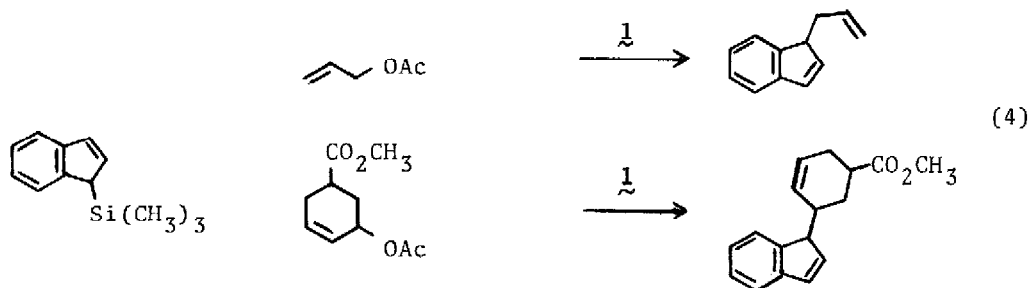
pathway would be most reasonable. The coupling reaction of allylstannanes is limited to those allyl acetates which cannot undergo such elimination reactions to form dienes.

References

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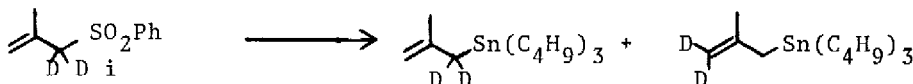
rapid allyl rearrangement of allylstannanes[4] leads to such an expectation. Their regioselectivity is thus best rationalized as resulting from thermo-dynamic equilibration of the initial products which would lead to exclusive formation of the product with tin at the primary carbon, as observed[4].
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