Vinylation of Aryl Bromides Using an Inexpensive Vinylpolysiloxane

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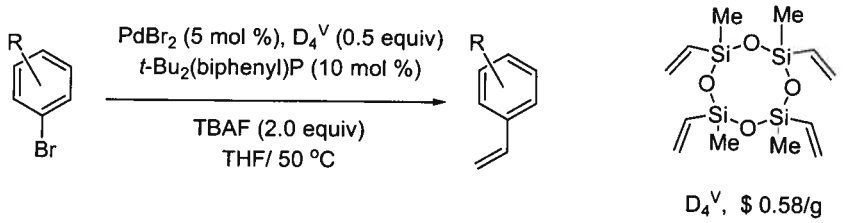
Substituted styrenes are important building blocks in fine chemical and polymer synthesis. Whereas classical preparations of styrenes involve harsh reaction conditions, the advent of transition-metal cross-coupling reactions allows for the direct synthesis of more functionally diverse styrenes. Here, we report the development of a mild method for the palladium-catalyzed vinylation of aryl bromides. The use of tetrabutylammonium fluoride (TBAF) as an activator and an inexpensive and non-toxic vinyl donor, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^V), allows for a general and high yielding preparation of substituted styrenes.



D_4^V, $ 0.58/g

Mechanism of the Lantibiotic Cyclase Involved in Nisin Biosynthesis

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Nisin is a ribosomally synthesized and posttranslationally modified antimicrobial peptide that, despite worldwide use for decades in the food industry, has not induced widespread resistance. It contains five cyclic thioether crosslinks of varying sizes that are installed by a single enzyme, NisC. Although the biosynthetic gene cluster of nisin was sequenced in 1989,[1] to date in vitro reconstitution of its biosynthesis, and that of other type I lantibiotics, has been unsuccessful. We present here the in vitro enzymatic synthesis of nisin A, which is shown to be bioactive by bacteria inhibition assay. We also investigate the mechanism of thioether ring formation using the thiol modifying agent PMBA. Five free thiols are present in the dehydrated peptide, which is the substrate for NisC. After the dehydrated peptide is treated with NisC, the peptide has no free thiols as a result of five cyclizations. The X-ray crystal structure of NisC provides further insights into the molecular mechanism of nisin biosynthesis. Intriguingly, the bacterial enzyme bears similarities in fold and substrate activation with mammalian farnesyl transferases, which may have implication for the human homologs of NisC.

[1] Kaletta, C.; Entian, K. D. *J. Bacteriol.* **1989**, *171*, 1597-601.