FROM ESTERS TO ALDEHYDES AND BEYOND: TRIARYLBORANE-CATALYZED HYDROSILYLATION

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Ester-to-aldehyde reduction remains a persistent challenge in organic synthesis. Although aluminum hydride reagents can effect this transformation, their limited chemoselectivity and poor functional-group tolerance restrict broader application. Catalytic hydrosilylation has recently emerged as an alternative strategy, proceeding via silylacetal intermediates.

This presentation describes our recent advances in triarylborane-catalyzed ester hydrosilylation. Systematic structure–reactivity studies have enabled the extension of this methodology to a diverse set of polyfunctional ester substrates. Beyond serving as intermediates en route to aldehydes, the resulting silyl acetals are shown to function as synthetically useful aldehyde surrogates in downstream transformations.

Mechanistic studies, supported by DFT calculations, reveal unconventional catalytic pathways underlying this process. Notably, subtle modifications to the ester substrate, catalyst structure, or silane reagent can induce pronounced changes in reaction outcome, leading to divergent product formation.