The Hosomi–Sakurai Reaction

Selected examples:

- 70% yield
- 96% yield
- 72% yield (cis/trans = 37:63)
- 54% yield
- 58% yield *BF₃·OEt₂ used as Lewis acid

Simplified mechanism:

Significance: The Hosomi–Sakurai reaction is a powerful synthetic tool used to add a nucleophilic allyl group to ketones and aldehydes under Lewis-acidic conditions. In this original 1976 report of the reaction, Hosomi and Sakurai illustrate a truly remarkable scope, adding allyltrimethylsilane to a variety of carbonyl-containing compounds, using only TiCl₄, with reaction times typically being under ten minutes. The reaction typically worked best with alkyl-derived aldehydes, though ketones and benzaldehyde were amenable to the reaction. In the case of benzaldehyde, BF₃·OEt₂ was used as the Lewis acid.

Comment: The Hosomi–Sakurai reaction initiates by coordination of the oxaphilic Lewis acid to the carbonyl group. Subsequent attack of the olefin forms a silyl-stabilized secondary β-cation. A nucleophilic source of halogen then attacks the TMS group, thereby generating a double bond. Since this report, a wide variety of catalytic and enantioselective variants of this reaction have been discovered (see Review below).