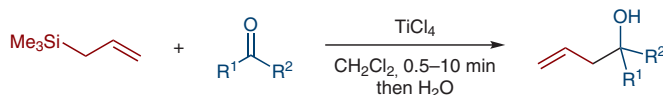


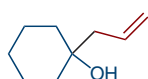
A. HOSOMI, H. SAKURAI* (TOHOKO UNIVERSITY, SENDAI, JAPAN)

Syntheses of γ,δ -Unsaturated Alcohols from Allylsilanes and Carbonyl Compounds in the Presence of Titanium Tetrachloride *Tetrahedron Lett.* **1976**, 17, 1295–1298, DOI: 10.1016/S0040-4039(00)78044-0.

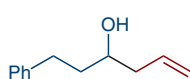
The Hosomi–Sakurai Reaction



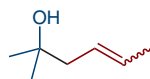
Selected examples:



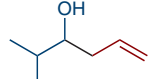
70% yield



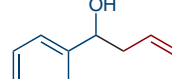
96% yield



72% yield
(*cis/trans* = 37:63)

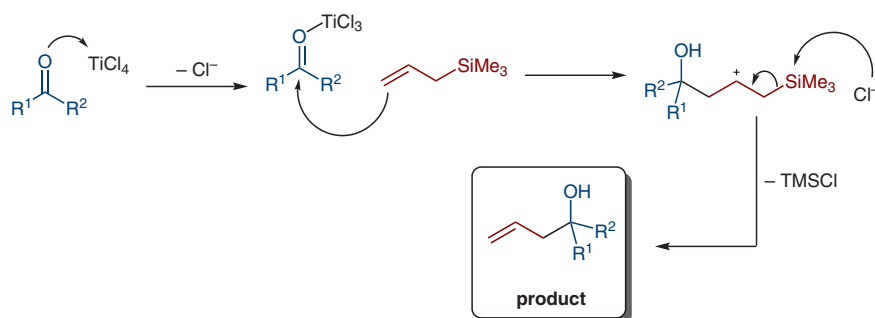


54% yield



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 oxophilic 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).

Review: J. J. Lade, S. D. Pardeshi, K. S. Vadagaonkar, K. Murugan, A. C. Chaskar *RSC Adv.* **2017**, 7, 8011–8033.