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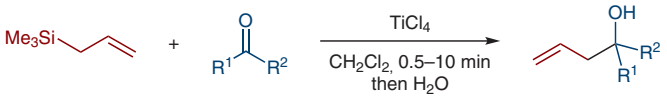
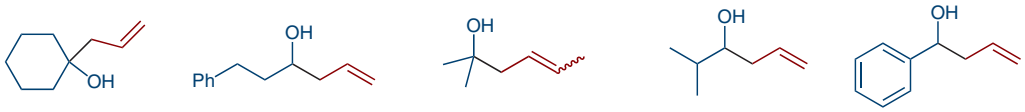
Syntheses of γ,δ-Unsaturated Alcohols from Allylsilanes and Carbonyl Compounds in the Presence of Titanium Tetrachloride
Tetrahedron Lett. **1976**, *17*, 1295–1298, DOI: 10.1016/S0040-4039(00)78044-0.

The Hosomi–Sakurai Reaction

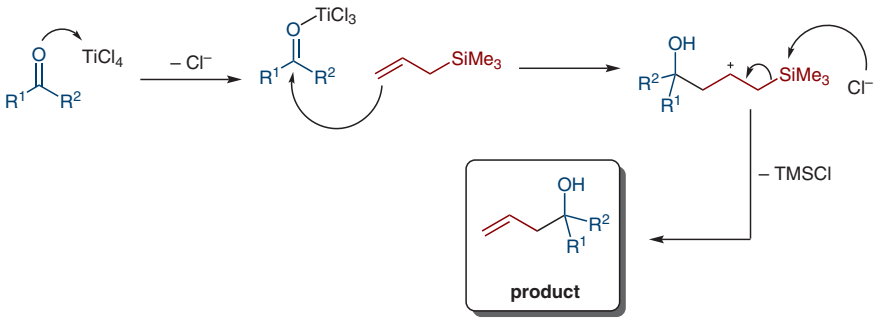


Selected examples:



70% yield | 96% yield | 72% yield (*cis*/*trans* = 37:63) | 54% yield | 58% yield *BF_3•OEt_2 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 $TiCl_4$, 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, $BF_3{\cdot}OEt_2$ 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).

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

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Metals in Synthesis

Key words
titanium catalysis
Lewis acids
allylation
organosilicon
carbonyl groups