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NCLEX-RN

CHEAT SHEET

Signs

HR: 60–100 bpm
RR: 12–20 rpm

BPM: 110–130/60 mmHg

T: 37 °C (98.6 °F)

Neurology Values

CSF: <5.0 million

EEG: 50–1000

ECG: 500,000–400,000

INR (Lab): 12–16 g/dL (Female); (Male): 10–14 g/dL

PT (Lab): 17–47 (Female); 40–50 (Male)

Electrolytes

Na⁺: 135–145 mEq/L

K⁺: 3.5–5.0 mEq/L

Cl⁻: 95–105 mEq/L

HCO₃⁻: 21–25 mEq/L

Ca²⁺: 8.5–10.2 mg/dL

Mg²⁺: 1.5–2.5 mg/dL

P: 8.5–10.5 mg/dL

Glucose: 80–120 mg/dL

BUN: 8–18 mg/dL

Cr: 0.5–1.0 mg/dL

Urea: 10–20 mg/dL

High-Yielding and Rapid Carbon–Carbon Bond Formation from Alcohols: Allylation by Means of TiCl_4

Alfred Hassner,* Chennakesava Reddy Bandi

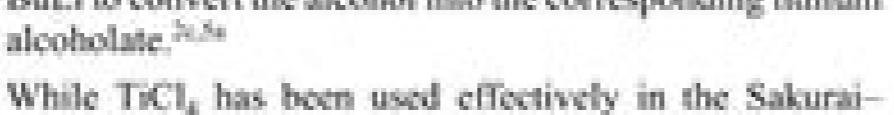
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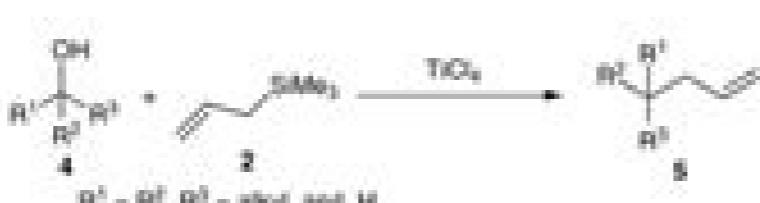
Abstract: TiCl₄ efficiently promotes high yield (80–99%) replacement of OH in tertiary, benzylic, and allylic alcohols, and even non-activated secondary alcohols, by an allyl group. The reaction usually proceeds within minutes at room temperature.

Key words: alcohols, C-C bonds, allylation, allyltrimethylsilane, Lewis acid, TiCl₄

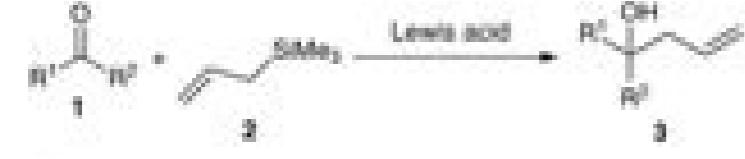
Carbon–carbon bond-forming reactions are important tools for the synthesis of organic compounds. Ketones and alcohols are particularly useful substrates for the introduction of allyl functional groups. In addition to the reaction of aldehydes or ketones with Grignard and other organometallic reagents, the Lewis acid¹ catalyzed allylation of such compounds involving nucleophilic transfer of an allyl group from an allyl silane (Sakurai–Hosomi allylation, Scheme 1)¹ has been of major importance.



Hosomi allylation of aldehydes and ketones,¹ to the best of our knowledge there has been only one report of the replacement of OH by an allyl group in the presence of TiCl₄.² We therefore examined the application of TiCl₄ to



Scheme 2

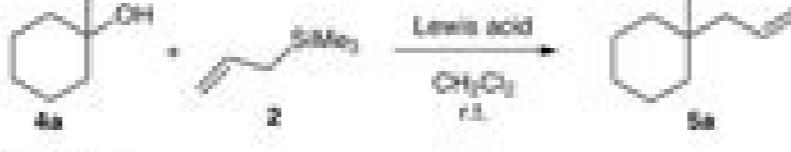


Scheme

Recently, the Sakurai–Hosomi allylation has inspired the development of C-allylation of alcohols (replacement of OH by an allyl group), especially of benzylic or tertiary alcohols using allyltrimethylsilane **2**.^{2–12}

Generation of allylated carbon from alcohols by means of allylsilanes has been reported in the presence of a variety Lewis acids based on B,³ In,³ Bi,⁴ Fe,⁵ Al,⁶ Ca,⁷ Zr,⁸ Re,⁹ Rh,¹⁰ as well as montmorillonites¹¹ and phosphomolybdic acid (PMA),¹² used either in catalytic or stoichiometric amounts. The yields are variable, and the reactions sometimes required hours and/or heating. Thus, using InCl₃ and allylsilanes, Baba et al.¹³ have successfully converted benzylic alcohols into allyl derivatives in 50–90% yield with reaction times of ten minutes to 7.5 hours. They further showed that by first converting the alcohols into silyl ethers¹⁴ and using InCl₃/I₂ or InCl₃/TMSBr,^{14,15} the OTMS group was more readily displaced than the OH group by an allyl moiety. Allyl-group introduction using allyltrimethylsilane and FeCl₃ was also carried out by first using

First we examined the reaction of 1-methylcyclohexanol (**4a**), a tertiary alcohol as a substrate in the reaction with allyltrimethylsilane **2**, and compared $TiCl_4$ with several other Lewis acids and with TsOH. We found $TiCl_4$ to be superior not only in terms of the yield of allylated product **5** but also in that it requires shorter reaction times and proceeds at room temperature (Table 1 and Scheme 3). Allyl-trichlorosilane was much less effective.



Scheme 2

We then examined several other alcohols and report (Table 2) that $TiCl_4$ is very effective in converting activated alcohols (tertiary or benzylic) **4** in high yield (80–99%) into allyl derivatives **5** in 1–5 minutes at room temperature. Benzhydryl alcohols and triphenylmethanol, which can form a highly stabilized carbocation, reacted even faster (1–2 min) and provided products **5** in excellent yields while requiring only 0.1 equivalents of $TiCl_4$. Tertiary alcohols and secondary benzylic alcohols gave allylated products in over 90% yield within minutes. Allylic alcohol **4b** and even the primary benzyl alcohol **4b** reacted within 10–15 minutes and gave **5** in over 80% yield.

Amylylation of nonactivated *sec*-alcohols, except for norbornanol,¹⁴⁻¹⁷ (which can form a nonclassical carbocation), has not been reported. Using TiCl₄, we were able to con-

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