<table>
<thead>
<tr>
<th>Title</th>
<th>Sequential Amphiphilic Allylation of Aldimines with 2-Methylenepropane-1,3-diols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Kimura, Masanari; Tamaki, Takato; Tamaru, Yoshinao</td>
</tr>
<tr>
<td>Citation</td>
<td>Nagasaki Symposium on Nano-Dynamics 2008 (NSND2008), pp.44-45</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2008-01-29</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10069/9847">http://hdl.handle.net/10069/9847</a></td>
</tr>
<tr>
<td>Rights</td>
<td>NAOSITE: Nagasaki University’s Academic Output SITE</td>
</tr>
</tbody>
</table>
Sequential Amphiphilic Allylation of Aldimines with 2-Methylenepropane-1,3-diols

Masanari Kimura¹*, Takato Tamaki¹, Yoshinao Tamaru²
¹Graduate School of Science and Technology,
²Department of Applied Chemistry, Faculty of Engineering,
Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan
*Tel: +81-95-819-2679, Fax: +81-95-819-2684, E-mail: masanari@nagasaki-u.ac.jp

Key Words: Palladium, Triethylborane, Aldimine, Pyrrolidine, Amphiphilic Allylation

Abstract
The combination of Pd catalyst and triethylborane promotes amphiphilic allylation of aldime with 2-methylenepropane-1,3-diol in the order of nucleophilic-electrophilic attack to provide pyrrolidine under mild conditions.

Introduction
We have developed the first direct allylic activation of allyl alcohol promoted by Pd-catalyst and Et₃B. Et₃B activates allyl alcohol toward oxidative addition of a Pd(0) species by coordination to the hydroxy group to form π-allylpalladium, which serves as an allyl cation equivalent toward a variety of soft nucleophiles to cause electrophilic allylation (Tsui-Trost type reaction).¹ In the absence of nucleophiles, π-allylpalladium is subjected to an allyl-ethyl exchange reaction, providing allyl diethylborane as an allyl anion equivalent, which reacts with benzaldehyde or aldimes to provide homoallyl alcohols² or homoallylamines,³ respectively (umpolung of π-allylpalladium) (Scheme 1). Here we would like to report the sequential amphiphilic allylation of aldimes with 2-methylenepropane-1,3-diol in the order of nucleophilic-electrophilic allylation to provide 3-methylenepyrrrolidines under similar catalytic system.
Experimental

The reaction was conducted as follows: in situ formation of aldimines prepared from aldehydes and amines via azotropic distillation of THF-H₂O two times, and exposure of the aldimines residue to a mixture of 2-methylene-propane-1,3-diol, Pd(OAc)_2, n-Bu_3P, and Et_3B at 50 °C under nitrogen atmosphere. The representative results are summarized in Table 1 and Scheme 2.

### Results and Discussions

The reaction tolerates a wide variety of aldimines, except for the combination of aliphatic aldehyde and aliphatic amines. Et_2Zn is also effective for the amphiphilic allylation of aldimines with 1,3-dibenzyloxy-2-methylene-propan in the presence of Pd catalyst under mild conditions. On the contrary to the result of 2-methylene-propane-1,3-diol with Et_3B (run 4 in Table 1), Et_2Zn promotes the amphiphilic allylation of the aldimine composed of cyclohexanecarboxyaldehyde and cyclohexylamine to provide 3-methylene-pyrrolidine at room temperature in quantitative yield (Scheme 3).

### Conclusions

The catalytic system of Pd catalyst and triethylborane promotes aldimines to undergo the sequential amphiphilic allylation with 2-methylene-propane-1,3-diols. This reaction would be utilized for the efficient synthesis of physiologically active molecules, pyrrolidine and proline derivatives.

### References