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Synthesis of Pyrrole Derivatives by the Heck-Type Cyclization of γ,δ-Unsaturated Ketone O-Pentafluorobenzoyloximes  

The Narasaka–Heck Cyclization

\[
\begin{align*}
\text{R1} & = \text{Alk, Ar, CO2R} \\
\text{R2} & = \text{H, Alk, CO2R}
\end{align*}
\]

**Proposed mechanism:**

1. **Protodecarboxylation**
2. **Reductive elimination**
3. **Oxidative addition**
4. **Isomerization**
5. **Aromatization**
6. **Beta-hydride elimination**
7. **Syn-imino-palladation**

**Selected examples:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhHNPh</td>
<td>81%</td>
</tr>
<tr>
<td>EtO2CEt</td>
<td>45%</td>
</tr>
<tr>
<td>PhHNPhCO2Et</td>
<td>75%</td>
</tr>
<tr>
<td>PhHNPhCO2Et</td>
<td>88%</td>
</tr>
<tr>
<td>PhHNPh</td>
<td>78%</td>
</tr>
</tbody>
</table>

**Significance:** Based on the finding that palladium(0) can cleave the N–O bond of sulfonyloximes, Tsutsui and Narasaka reported a catalytic protocol coupled with an intramolecular Heck-type cyclization to form pyrroles. Competing Beckmann rearrangement of the oxime derivatives could be suppressed by changing from the sulfonyl- to the pentafluorophenylacetyl N-protecting group.

**Comment:** In the following years, this method was successfully extended to access various N-heterocycles (see Review below). An enantioselective version for the synthesis of dihydropyrroles bearing a stereogenic center at the 2-position was introduced by Bower and co-workers (Chem. Sci. 2017, 8, 1981).