H. TSUTSUI, K. NARASAKA* (THE UNIVERSITY OF TOKYO, JAPAN)
Synthesis of Pyrrole Derivatives by the Heck-Type Cyclization of γ,δ-Unsaturated Ketone O-Pentafluorobenzoyloximes

The Narasaka–Heck Cyclization

\[
\begin{align*}
\text{R}^1 & = \text{alk, ar, CO}_2\text{R} \\
\text{R}^2 & = \text{H, alk, CO}_2\text{R}
\end{align*}
\]

Proposed mechanism:

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).