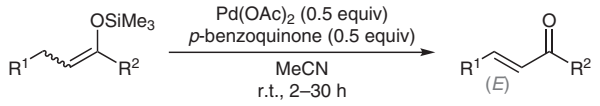
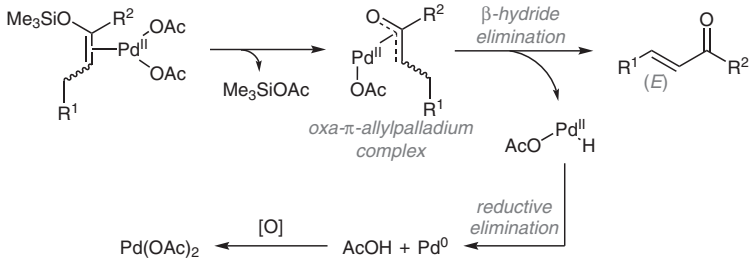
Y. ITO, T. HIRAO, T. SAEGUSA* (KYOTO UNIVERSITY, JAPAN)

Synthesis of α,β-Unsaturated Carbonyl Compounds by Palladium(II)-Catalyzed Dehydrosilylation of Silyl Enol Ethers
J. Org. Chem. **1978**, *43*, 1011–1013, DOI: 10.1021/jo00399a052.

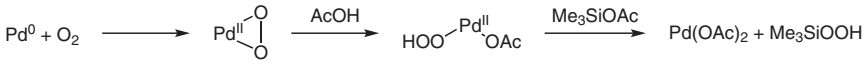
The Saegusa–Ito Oxidation of Silyl Enol Ethers to α,β-Unsaturated Carbonyl Compounds



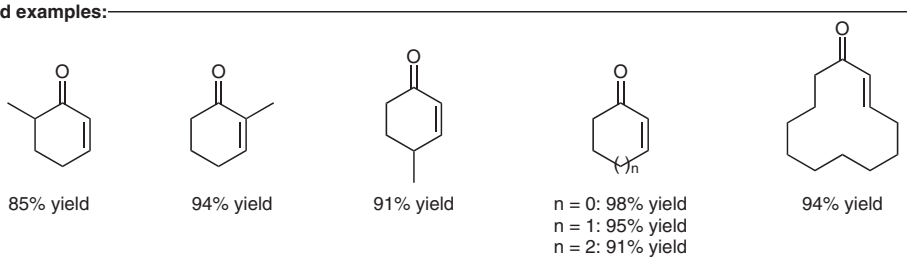
Proposed mechanism:

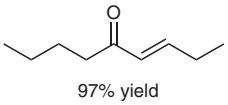


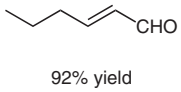
Larock modification: catalytic in $Pd(OAc)_2$

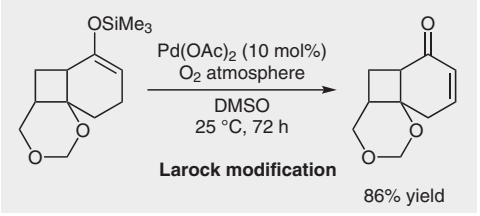


Selected examples:









Significance: The Saegusa–Ito oxidation, introduced in 1978, is a synthetically important transformation, allowing to convert silyl enol ethers into the corresponding α,β-unsaturated carbonyl compounds. With acyclic and large ring substrates, the reaction is completely stereoselective towards the *E*-isomer, regardless of the stereochemistry of the starting silyl enol ether.

Comment: The original reaction was barely substoichiometric, using 0.5 equiv of $Pd(OAc)_2$ and *p*-benzoquinone as the oxidant. Reducing the catalyst loading would systematically result in lower yields. One way to circumvent this drawback is the Larock modification (*Tetrahedron Lett.* **1995**, *36*, 2423). In this protocol, the reaction is carried out in DMSO under an oxygen atmosphere, which reoxidizes Pd(0) back to $Pd(OAc)_2$.

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Synfacts 2023, 19(08), 0799 Published online: 14.07.2023
DOI: 10.1055/s-0042-1752838; **Reg-No.:** M10423SF

Category
Metals in Synthesis

Key words
palladium catalysis
silyl enol ethers
α,β-unsaturated carbonyls