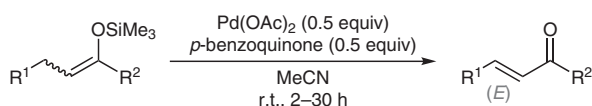


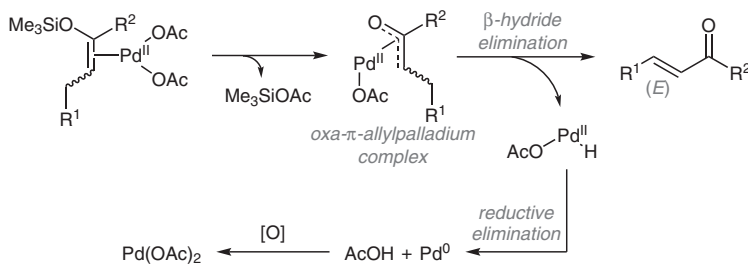
Y. ITO, T. HIRAO, T. SAEGUSA\* (KYOTO UNIVERSITY, JAPAN)

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

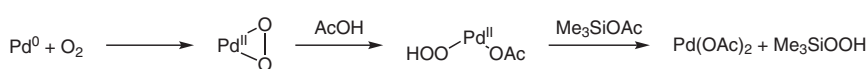
## The Saegusa–Ito Oxidation of Silyl Enol Ethers to $\alpha,\beta$ -Unsaturated Carbonyl Compounds



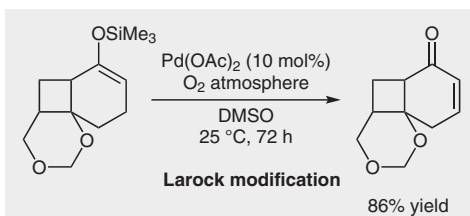
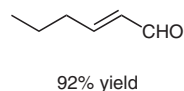
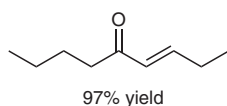
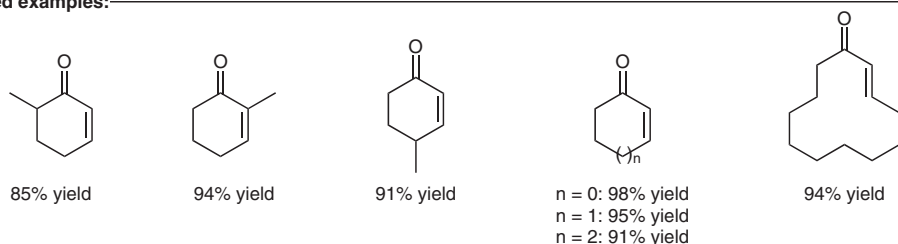
— Proposed mechanism:



Larock modification: catalytic in  $\text{Pd(OAc)}_2$



— Selected examples:



**Significance:** The Saegusa–Ito oxidation, introduced in 1978, is a synthetically important transformation, allowing to convert silyl enol ethers into the corresponding  $\alpha,\beta$ -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 sub-stoichiometric, using 0.5 equiv of  $\text{Pd(OAc)}_2$  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  $\text{Pd(0)}$  back to  $\text{Pd(OAc)}_2$ .

SYNFACTS Contributors: Martin Oestreich, Hendrik F. T. Klare, Emilio Acuña Bolomey  
Synfacts 2023, 19(08), 0799 Published online: 14.07.2023  
DOI: 10.1055/s-0042-1752838; Reg-No.: M10423SF

© 2023, Thieme. All rights reserved.  
Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

Category

Metals in Synthesis

Key words

palladium catalysis

silyl enol ethers

$\alpha,\beta$ -unsaturated carbonyls

Synfact  
Classic

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.