

Discovery

RESEARCHES UPON THE PHENOMENA OF OXIDATION AND CHEMICAL PROPERTIES OF GASES.

BY FRANCIS C. PHILLIPS.

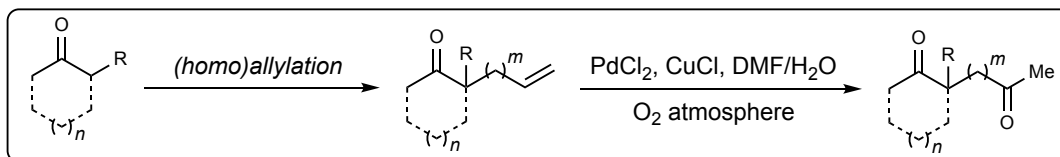
Discovered by Phillips in 1894 – “The reaction between palladium chloride and ethylene leads to the production of aldehyde”
Later (1959), researchers at Wacker Chemie reported catalytic palladium can be used with CuCl₂ and oxygen

Katalytische Umsetzungen von Olefinen an Platinmetall-Verbindungen

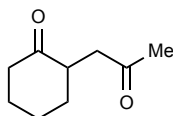
Das Consortium-Verfahren zur Herstellung von Acetaldehyd

Application in organic synthesis

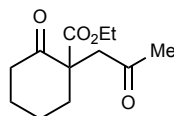
“Despite great industrial success, application of this unique oxidation method to general organic synthesis has not been explored.” – Tsuji, 1976



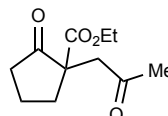
1,4-diketones:



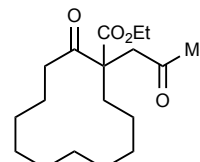
68%



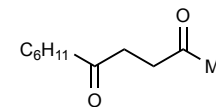
77%



71%

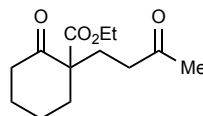


74%

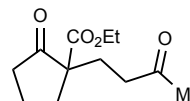


69%

1,5-diketones:



58%



61%

Phillips, F. C. *Am. Chem. J.* **1894**, 16, 255

Tsuji, J. *Tet. Lett.*, **1976**, 17 (34), 2975

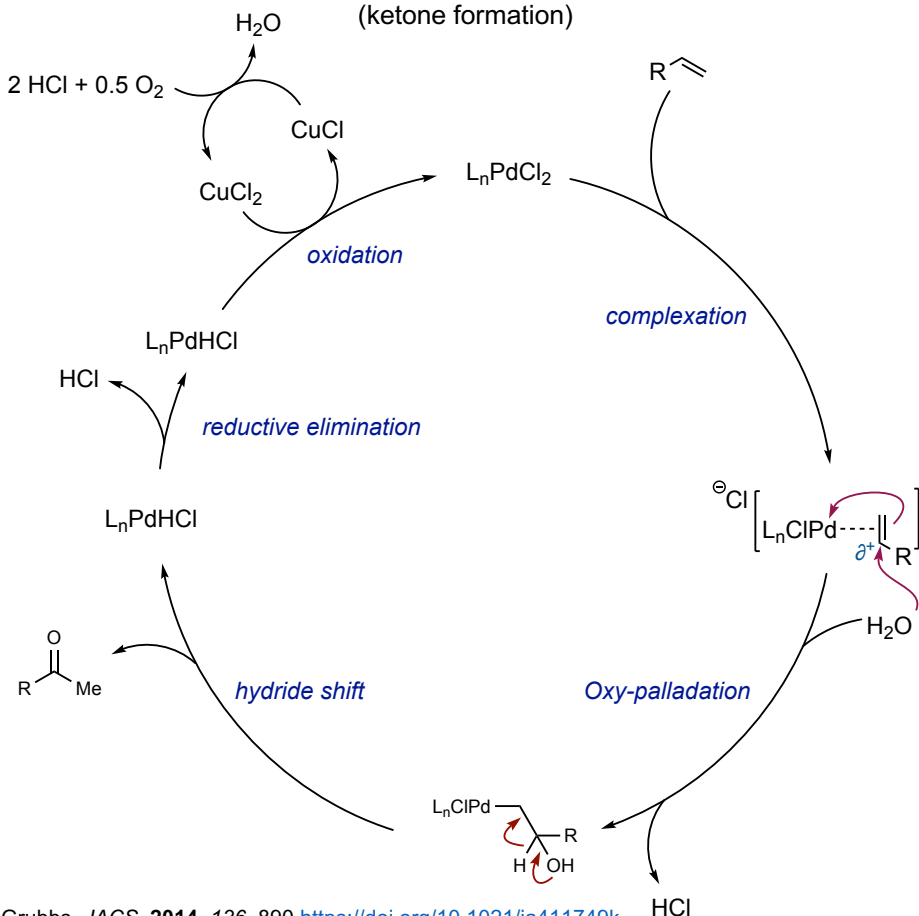
[https://doi.org/10.1016/S0040-4039\(01\)85504-0](https://doi.org/10.1016/S0040-4039(01)85504-0)

Proposed Mechanism

Decades of work have gone into the investigation of the mechanism of this reaction!

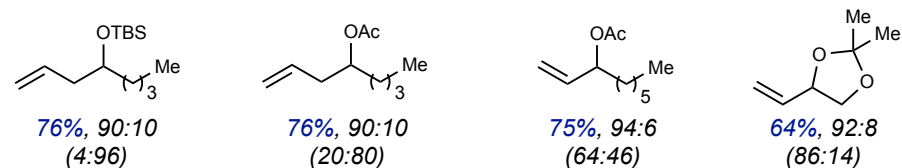
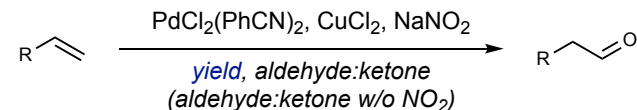
A simplified mechanism is depicted below, but the exact mechanism of oxypalladation and ketone formation have been debated extensively.

Partial positive charge causes oxygenation at the more substituted carbon (ketone formation)

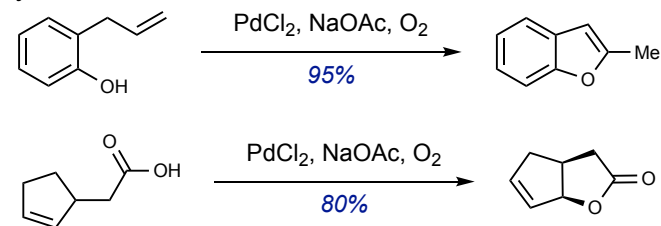


Other Applications

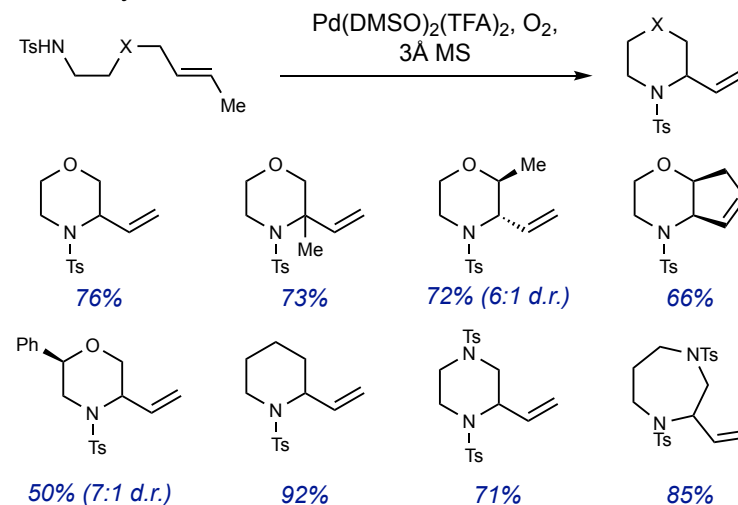
Grubbs-Wacker (Aldehyde-selective)

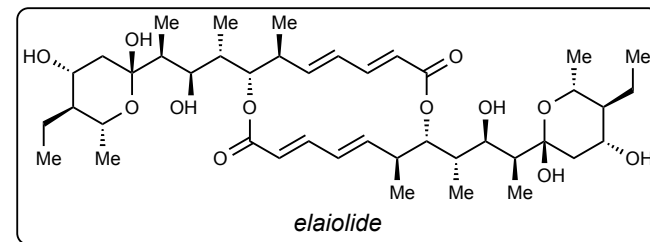
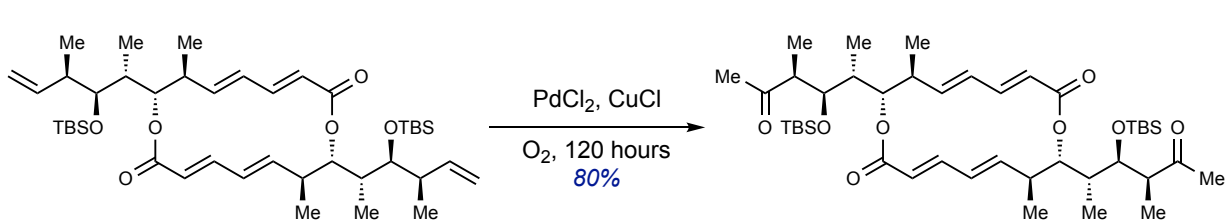


Wacker Cyclization

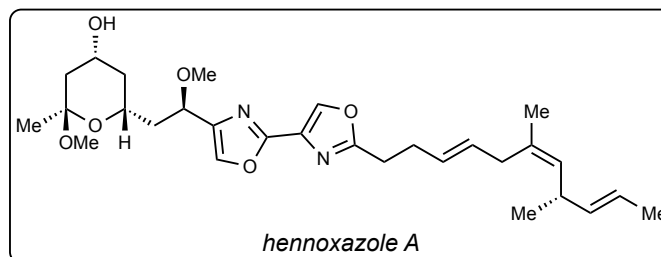
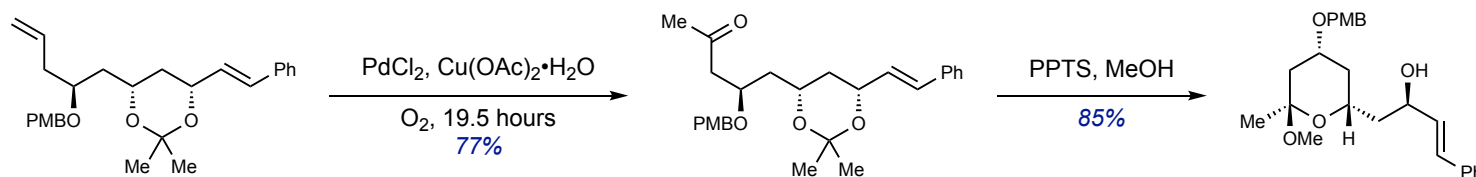


Aza-Wacker Cyclization

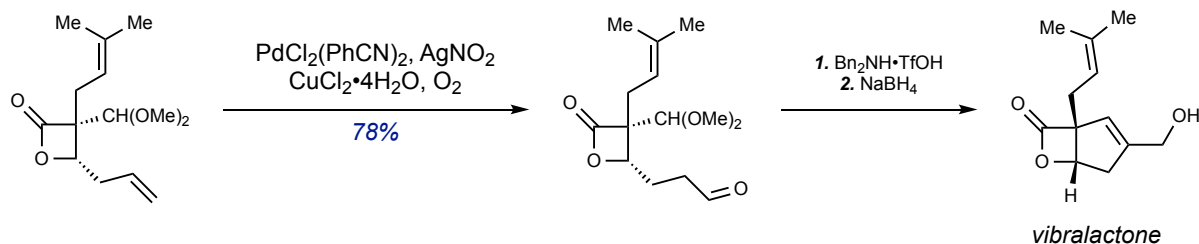




Mulzer, *Tetrahedron*, **2008**, 64, 4718 <https://doi.org/10.1016/j.tet.2008.01.114>



Yokokawa, *Tetrahedron*, **2001**, 57, 6311 [https://doi.org/10.1016/S0040-4020\(01\)00593-2](https://doi.org/10.1016/S0040-4020(01)00593-2)



Brown, *Org. Lett.* **2016**, 18, 5971 <https://doi.org/10.1021/acs.orglett.6b03007>