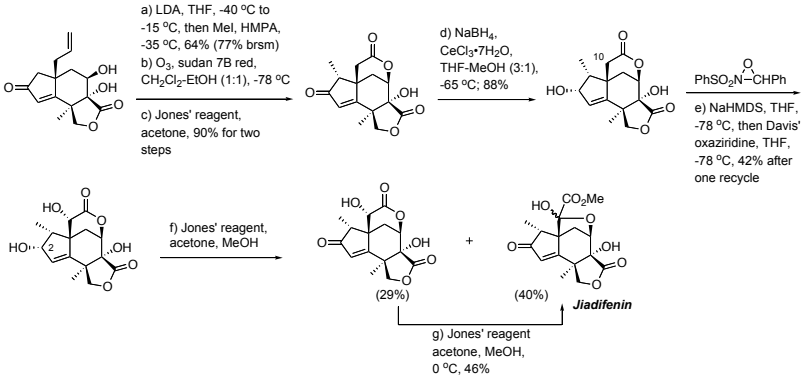
Oxidations

- *Jones Oxidation; PCC*
- *Swern Oxidation*
- *Dess-Martion Periodinane*
- *TPAP*
- *Sharpless Epoxidation*
- *Dihydroxylations*
- *Peracids*
- *Baeyer-Villiger Oxidation*
- *Ozonolysis*

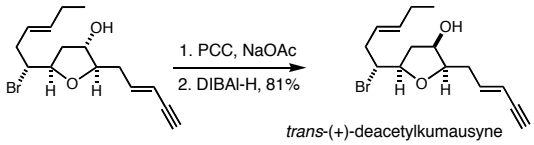
Oxidation of Alcohols to Acids [Jones]

Carcache, D. A.; Cho, Y. S.; Hua, Z.; Tian, Y.; Li, Y.-M.; Danishefsky, S. J., "Total synthesis of (+-)-jiadifenin and studies directed to understanding its SAR: Probing mechanistic and stereochemical issues in palladium-mediated allylation of enolate-like structures." *J. Am. Chem. Soc.* **2006**, *128*, 1016-1022.



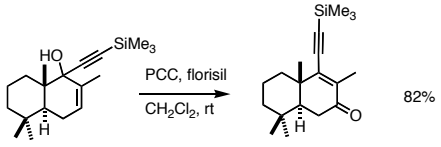
PCC Oxidation

- Martin, T.; Soler, M. A.; Betancort, J. M.; Martin, V. S. *J. Org. Chem.* **1997**, *62*, 1570.

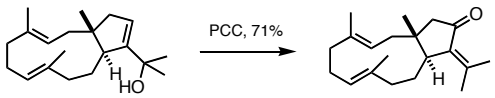


trans-(+)-deacetylkumausyne

- PCC can also be used to effect the rearrangement/oxidation of tertiary allylic alcohols (THL **1998**, *39*, 6521).

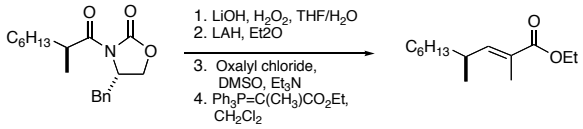


- Corey, E. J.; Kania, R. S. *Tetrahedron Lett.* **1998**, *39*, 741.



Oxidation of 1° Alcohols to Aldehydes [Swern]

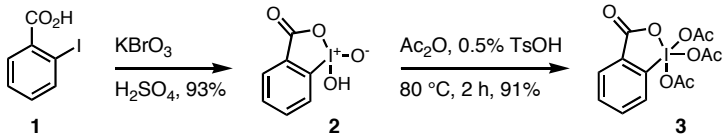
Wipf, P.; Kim, Y.; Fritch, P. C. *J. Org. Chem.* **1993**, *58*, 7195.



Wipf, P.; Xu, W. *J. Org. Chem.* **1996**, *61*, 6556.

Alcohol to Aldehyde or Ketone [Dess-Martin]

- Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277. The Dess-Martin periodinane **3** is an extremely useful reagent for the conversion of primary and secondary alcohols to aldehydes and ketones at 25 °C. It does not overoxidize aldehydes to carboxylic acids under these conditions and tolerates the presence of furan rings or sulfides and vinyl ethers. It reacts with primary amines to give insoluble products, and reacts slowly enough with secondary amines and sulfides to make it possible to oxidize alcohols in the presence of these functional groups.



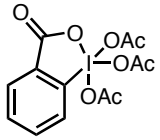
1 **2** **3**

In 1993, Ireland and Liu reported an improved procedure for the preparation of the Dess-Martin periodinane (*J. Org. Chem.* **1993**, *58*, 2899). **CAUTION! Precursor oxide 2 (IBX) was reported to be explosive under excess heating!**

Boeckman, R. K., Jr.; Shao, P.; Mullins, J. J., "The Dess-Martin periodinane: 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one." *Org. Synth.* **2000**, *77*, 141-152.

Dess-Martin Oxidation

- Impure samples of Dess-Martin periodinane may in many cases provide better results than the pure reagent, since the partially hydrolyzed agent is a more effective oxidant. However, the fully hydrolyzed material is a polymer that seems to have deactivating effects that result in the requirement of multiple equivalents of reagent. Accordingly, when rate enhancement is desired, the pure oxidant may be decomposed with one equivalent of water immediately before or during its use (Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7549).

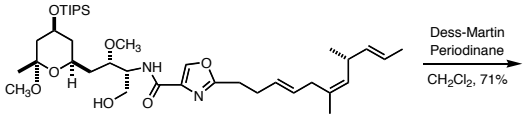


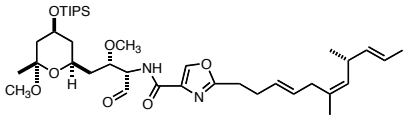
Racemization is minimized with DMP: Myers, A. G.; Zhong, B.; Movassaghi, M.; Kung, D. W.; Lanman, B. A.; Kwon, S., "Synthesis of highly epimerizable N-protected α-amino aldehydes of high enantiomeric excess." *Tetrahedron Lett.* **2000**, *41*, 1359-1362.

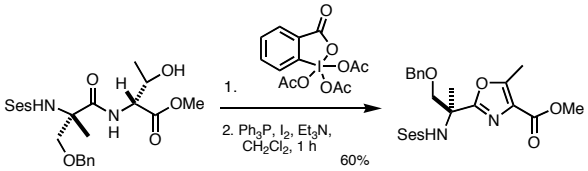
Dess-Martin Oxidation

- Wipf, P.; Lim, S. *J. Am. Chem. Soc.* **1995**, *117*, 558; Wipf, P.; Lim, S. *Chimia* **1996**, *50*, 157.

- Wipf, P.; Miller, C. P. *J. Org. Chem.* **1993**, *58*, 3604.

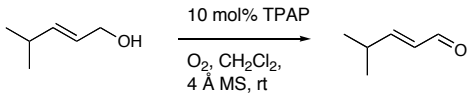






Oxidation of 1° Alcohols to Aldehydes [TPAP]

Lenz, R.; Ley, S. V. *Perkin Trans. 1* **1997**, 3291. Tetra-n-propylammonium perruthenate (TPAP)-catalyzed oxidations of alcohols using molecular oxygen as a co-oxidant. Aliphatic aldehydes lead to partial overoxidation to acids.



One of the advantages of TPAP is that it can be used in for amine-containing alcohols (see, for ex. Trauner, D.; Schwarz, J. B.; Danishefsky, S. J. *Angew. Chem. Int. Ed.* **1999**, *38*, 3542-3545).

- Ali, S. M.; Georg, G. I. *Tetrahedron Lett.* **1997**, *38*, 1703.