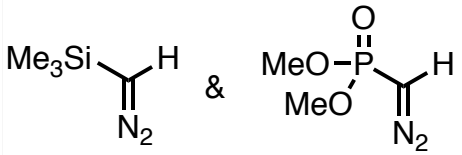
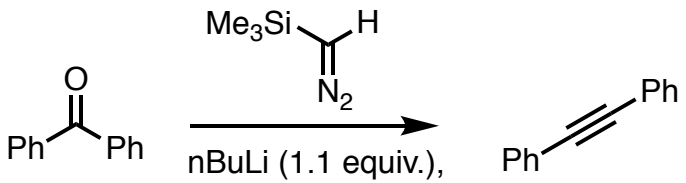
Seyferth-Gilbert Homologation/Bestmann-Ohira Reagent

Dietmar Seyferth
MIT (Emeritus)

Seyferth, **1971**



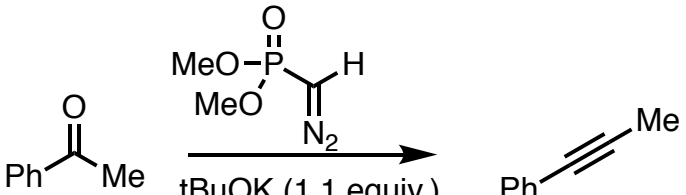
Colvin & Hamill, **1973**



*only non-enolizable ketones

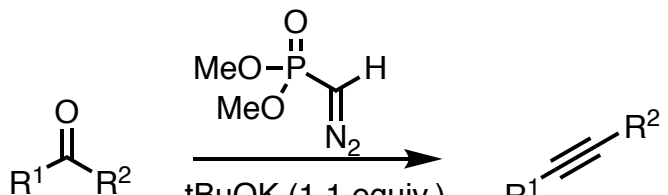
John Gilbert
UT-Austin (Emeritus)

Gilbert & Weeraooriya, **1979**



*can be used on enolizable ketones and aldehydes
*strongly basic conditions that may not be suitable for all substrates

Seyferth-Gilbert Homologation



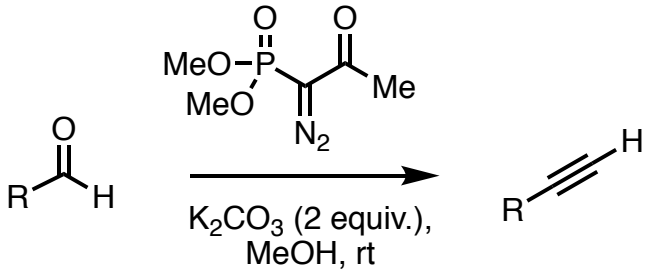
aldehyde or ketone

terminal or internal

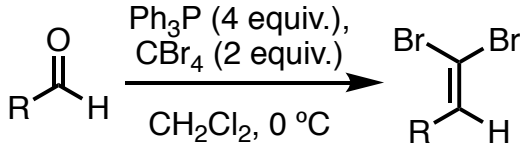
Seyferth, D.; *et al., J. Am. Chem. Soc.* **1967**, *89*, 4811. Colvin, E.W.; *et al., J.C.S. Chem. Comm.* **1973**, 151. Gilbert, J.C.; *et al., J. Org. Chem.* **1979**, *44*, 4997.

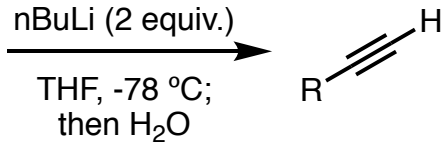
Seyferth-Gilbert Homologation/Bestmann-Ohira Reagent

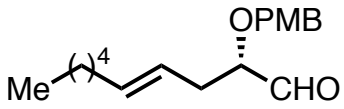
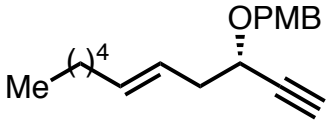
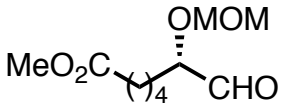
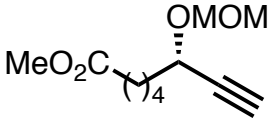
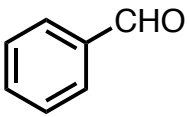
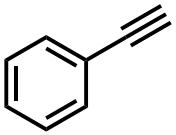
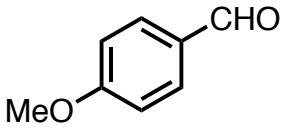
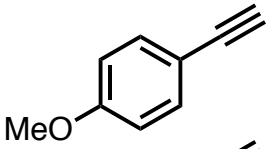
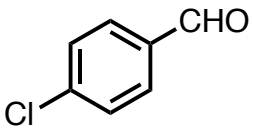
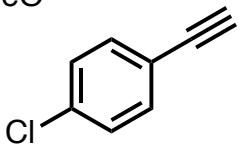
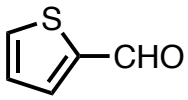
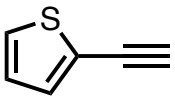
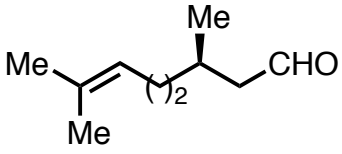
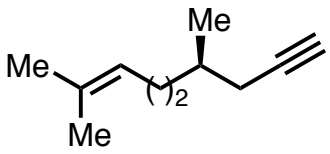
Bestman-Ohira Modification



related: Corey-Fuchs reaction



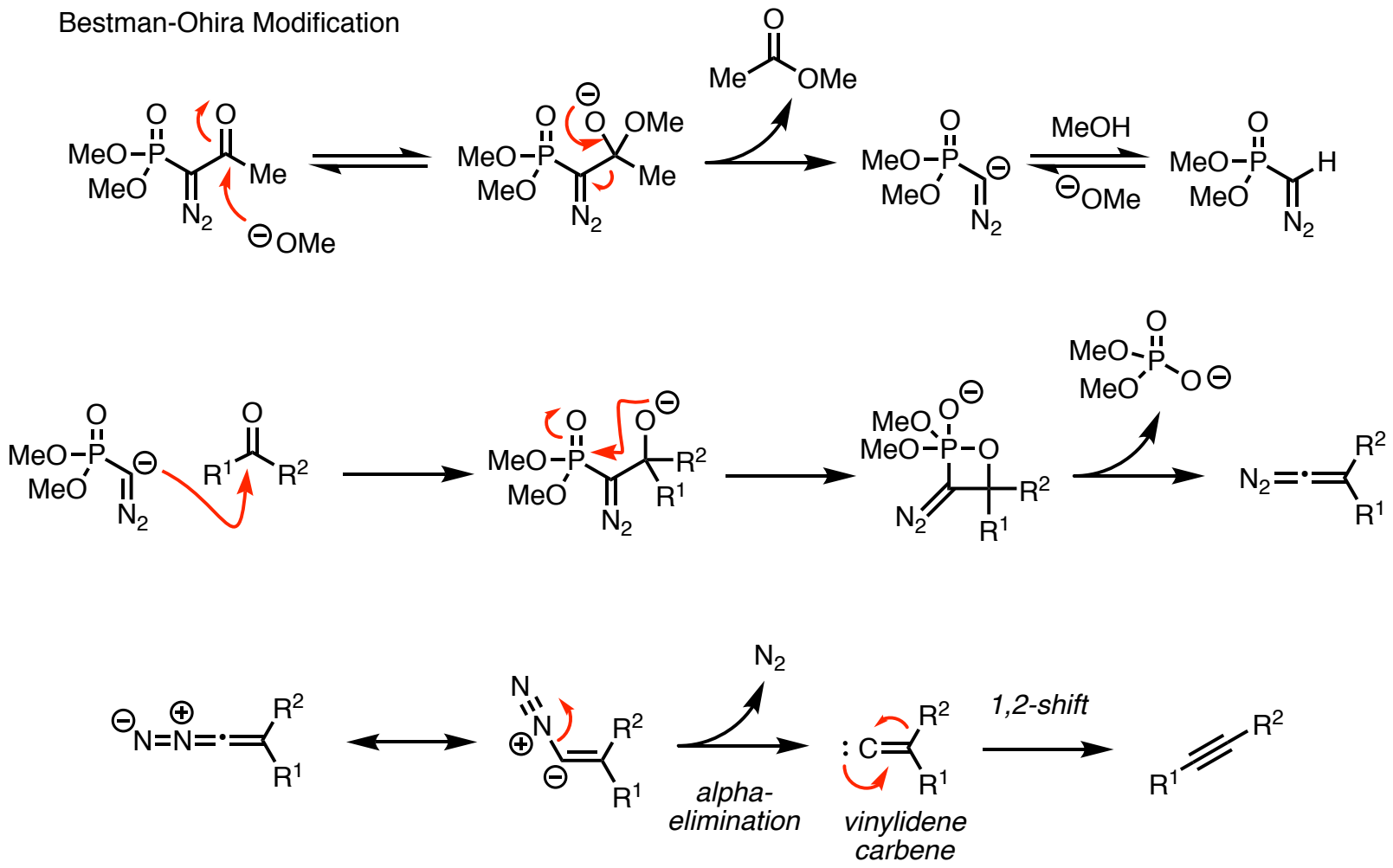


aldehyde	terminal alkyne	yield
		76%*
		83%*
		73%
		78%
		97%
		80%
		96%

*no observable degradation in enantiopurity

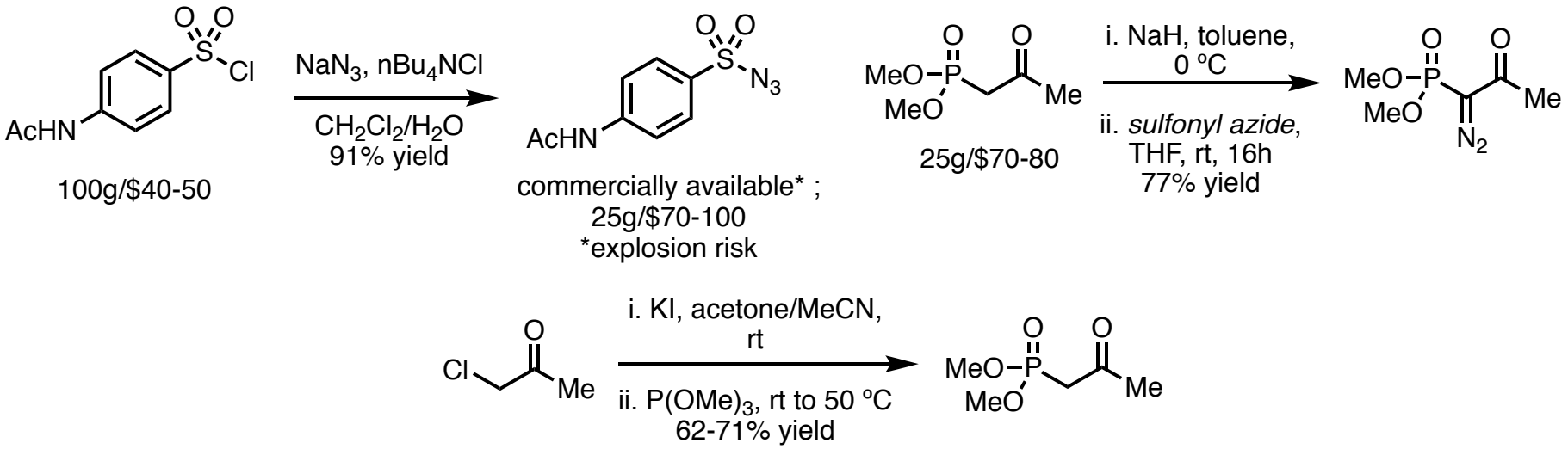
Ohira, S., *Synth. Comm.* **1988**, 561. Bestmann, H.J.; *et al., Synlett.* **1996**, *521.*

Mechanism of Homologation



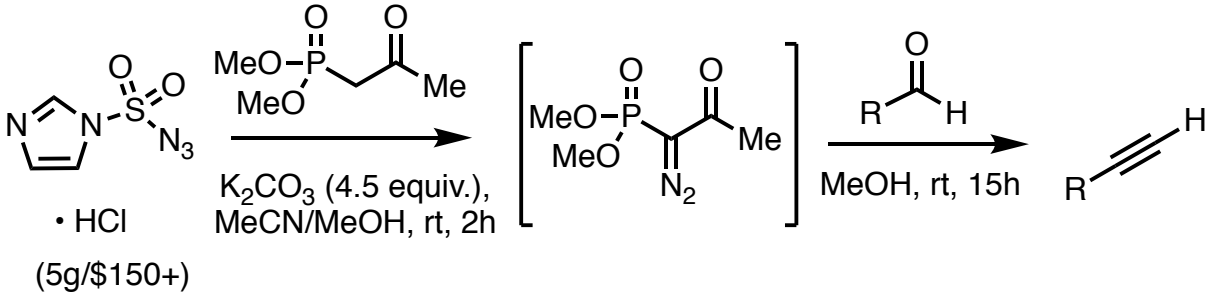
Bestmann-Ohira Reagent Synthesis

Peitruszka & Witt, **2006**



In situ Bestmann-Ohira Reagent Synthesis

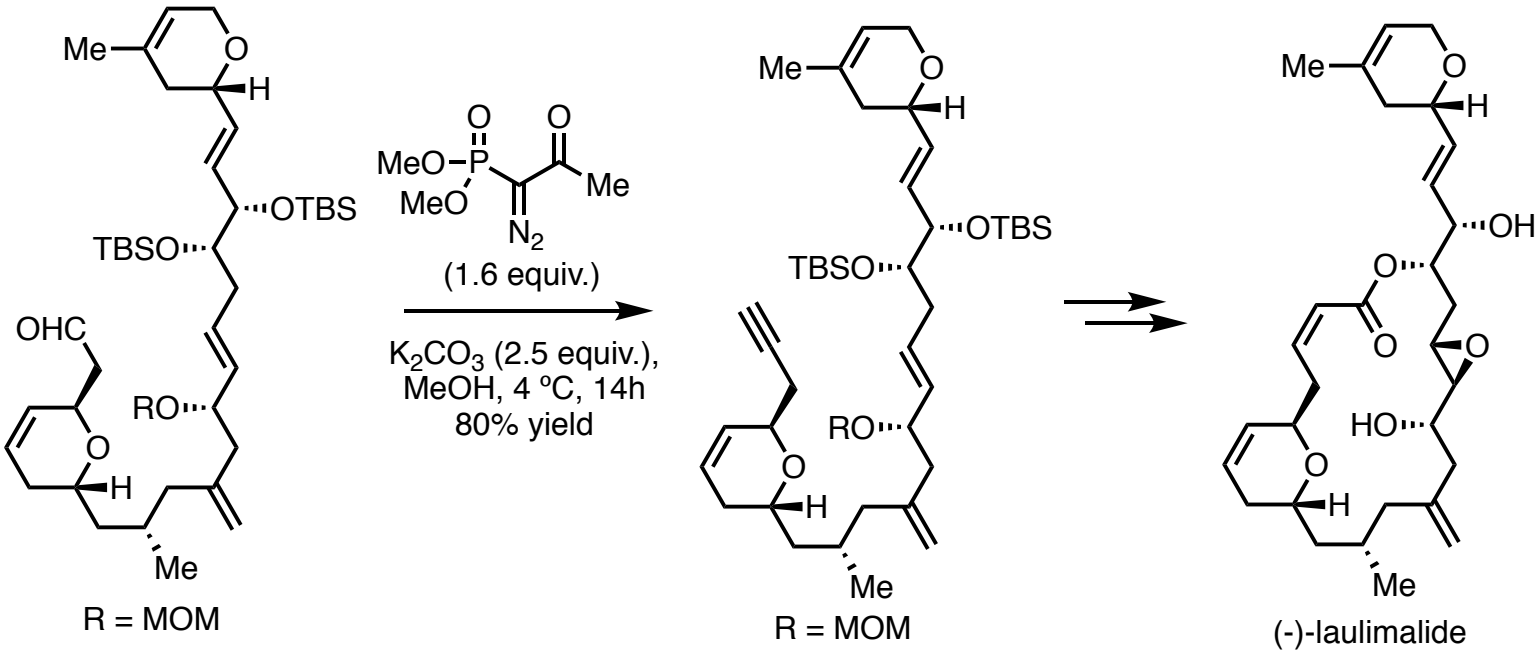
Kristensen & Jepsen, **2014**



Pietruszka, J.; Witt, A., *Synthesis* **2006**, *24*, 4266. Noyori, R.; *et al.*, *J. Am. Chem. Soc.* **1995**, *117*, 2931. Jepsen, T.H.; Kristensen, J.L., *J. Org. Chem.* **2014**, *79*, 9423.

Total Synthesis Example

Paul Wender, **2002**



Wender, P.A.; *et al., J. Am. Chem. Soc.* **2002**, *124*, 4956.