Category

Organo- and **Biocatalysis** 

**Key words** 

**Brønsted acids** 

phosphine oxide reduction chemoselective reduction

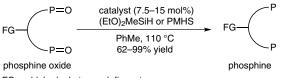
silanes

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Highly Chemoselective Metal-Free Reduction of Phosphine Oxides to Phosphines

J. Am. Chem. Soc. 2012, 134, 18325-18329.

## **Organocatalytic Chemoselective Reduction** of Phosphine Oxides to Phosphines



FG = aldehyde, ketone, olefin, ester PMHS = polymethylhydrosiloxane

## catalyst $R = H, O_2N, F_3C$

#### Proposed mechanism:

## HSiMe(OEt)<sub>2</sub> OSiMe(OEt)<sub>2</sub> silane disiloxane

$$R^{1} \stackrel{P}{\underset{R^{2}}{\vdash}} R^{3}$$
  $-H_{2}$   $R^{1} \stackrel{P}{\underset{R^{2}}{\vdash}} R^{3}$  phosphine oxide phosphine

### Selected examples of converted phosphine oxides:

86% yield

# 80% yield 88% yield

 $\dot{N}H_2$ 81% yield

#### Some examples of phosphines:

Significance: Organophosphines represent valuable intermediates, catalysts, and ligands for transition-metal catalysis. Here, the authors report the utilization of inexpensive silanes by Brønsted acid catalysis, which shows broad functional group tolerance towards aldehydes, ketones, olefins, nitriles, and esters. Chemoselectivities of 99:1 for P-O double bonds and retention of the configuration at the P-center were achieved.

 $\textbf{SYNFACTS Contributors:} \ Benjamin \ List, \ Philip \ S. \ J. \ Kaib$ Synfacts 2013, 9(1), 0099 Published online: 17.12.2012 DOI: 10.1055/s-0032-1317901; Reg-No.: B11412SF

Comment: The catalytic chemoselective reduction of P-O double bonds (502 kJ/mol) is a formifree protocol under convenient, air-insensitive, and safe reaction conditions for aryl, alkyl, monotional group tolerance indicates possible applications in catalytic Wittig, Appel, and Staudinger reactions.

dable challenge in synthetic chemistry. This metaland bidentate phosphine oxides with its high func-