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.

Comment: The catalytic chemoselective reduction of P–O double bonds (502 kJ/mol) is a formidable challenge in synthetic chemistry. This metal-free protocol under convenient, air-insensitive, and safe reaction conditions for aryl, alkyl, mono- and bidentate phosphine oxides with its high functional group tolerance indicates possible applications in catalytic Wittig, Appel, and Staudinger reactions.

Some examples of phosphines:

- 81% yield
- 73% yield
- 86% yield
- 90% yield
- 89% yield
- 89% yield

Selected examples of converted phosphine oxides:

- 86% yield
- 62% yield
- 88% yield
- 71% yield
- 92% yield
- 98% yield
- 99% yield

Proposed mechanism:

\[
\begin{align*}
\text{PhMe, 110 °C} & \quad 62–99\% \text{ yield} \\
\text{catalyst (7.5–15 mol\%)} & \quad \text{(EtO)₂MeSiH or PMHS} \\
\end{align*}
\]

\[
\begin{align*}
\text{FG} = \text{aldehyde, ketone, olefin, ester} \\
\text{PMHS = polymethylhydrosiloxane} \\
\text{FG} = \text{aldehyde, ketone, olefin, ester} \\
\text{PMHS = polymethylhydrosiloxane} \\
\end{align*}
\]