Massachusetts Institute of Technology Organic Chemistry 5.512

April 22, 2005 Wesley Austin

Problem Set 5 Solutions Stereocontrolled Addition to Carbonyl Compounds

(1) See also K. Buzek. J. Am. Chem. Soc. 1994, 116, 5511.

(2) See also D. A. Evans. J. Org. Chem. 1997, 62, 454.

(3) See also K. C. Nicolaou. J. Am. Chem. Soc. 1993, 115, 4419.

(4) See also Z. Jin. Org. Lett. 2001, 3, 1447.

(5) See also K. Krohn. Liebigs Ann. Chem. 1994, 167.

MeCHO

$$\begin{array}{c}
\text{Zn} \swarrow)_2 \\
\text{(-)-DAIB}
\end{array}$$
 $\begin{array}{c}
\text{O}_3; H_2O_2 \\
\text{HO}
\end{array}$
 $\begin{array}{c}
\text{HO}_3; H_2O_2 \\
\text{HO}
\end{array}$
 $\begin{array}{c}
\text{HO}_4; H_2O_2 \\
\text{HO}
\end{array}$
 $\begin{array}{c}
\text{HO}_4; H_2O_2; H_2O_$

(6) See also P. V. Ramachandran J. Org. Chem. 2001, 66, 2512.

$$\begin{array}{c} \text{HO} \\ \text{CO}_2\text{Me} \\ \\ \text{HO} \\ \end{array} \begin{array}{c} \text{1) 2 eq } t\text{-BuMe}_2\text{SiCI}, \\ \text{2,6 lutidine} \\ \text{2) LiOH} \\ \\ \end{array} \begin{array}{c} \text{$t\text{-BuMe}_2\text{SiO}$} \\ \\ \text{$t\text{-BuMe}_2\text{SiO}$} \\ \end{array} \\ \text{"A"} \\ \end{array}$$

(7) 1)
$$t\text{-BuMe}_2\text{SiCl}$$
 2,6 lutidine 2) LiAlH₄ 3) CBr₄, PPh₃ $t\text{-BuMe}_2\text{SiO}$ $t\text{-BuMe}_2\text{SiO}$ $t\text{-BuMe}_2\text{SiO}$ $t\text{-BuMe}_2\text{SiO}$

(9) See also J. Cossy. *Tetrahedron Lett.* **2000**, *41*, 3363.

OHC

Ph

$$\begin{array}{c}
1) \\
B(lpc)_2(+) \\
2) O_3; Me_2S \\
3) Et_3SiCl, Et_3N
\end{array}$$
OHC

Ph

$$\begin{array}{c}
0SiEt_3 \\
Ph
\end{array}$$
OHC

Ph

$$\begin{array}{c}
0SiEt_3 \\
2) O_3; H_2O_2
\end{array}$$
HO

Ph

$$\begin{array}{c}
0SiEt_3 \\
Ph
\end{array}$$
Ph

$$\begin{array}{c}
0 \\
1) TBAF \\
2) cat TsOH
\end{array}$$
HO

Ph

(10) See also Y. Kishi. Angew. Chem. Int. Ed. 1998, 37, 190.

OHC OSi(
$$i$$
-Pr)₃ $\xrightarrow{B(lpc)_2(-)}$ OBn OSi(i -Pr)₃ $\xrightarrow{2) i$ -Pr₃SiCl, $3) C_3$; Me₂S OHC OSi(i -Pr)₃ $\xrightarrow{2) i$ -Pr₃SiCl, $3) Li$, NH₃ OSi(i -Pr)₃