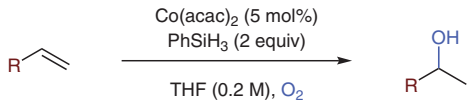
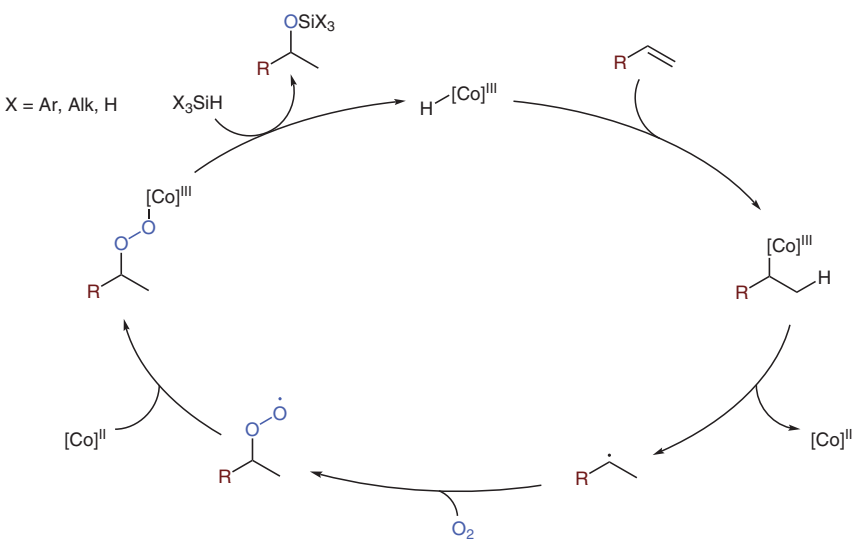
S. ISAYAMA, T. MUKAIYAMA* (MITSUI PETROCHEMICAL INDUSTRIES, LTD., JAPAN)
A New Method for Preparation of Alcohols from Olefins with Molecular Oxygen and Phenylsilane by the Use of Bis(acetylacetonato)cobalt(II)
Chem. Lett. **1989**, *18*, 1071–1074, DOI: 10.1246/cl.1989.1071.

Cobalt-Catalyzed Hydrohydroxylation of Olefins Using Molecular Oxygen – The Mukaiyama Hydration



Original examples:

Plausible mechanism:



Significance: In 1989, Isayama and Mukaiyama reported the room-temperature Markovnikov hydration of olefins using low loadings of $Co(acac)_2$, phenylsilane and molecular oxygen, more commonly known as the 'Mukaiyama hydration'. The Mukaiyama hydration has been widely used in total synthesis and is still one of the most effective strategies to enable a Markovnikov hydration of alkenes.

Review: J. E. Zweig, D. E. Kim, T. R. Newhouse *Chem. Rev.* **2017**, *117*, 11680–11752.

Comment: Previous cobalt-catalyzed hydration protocols used 2° alcohols as the hydride source; however, they required a higher catalyst load and temperature. The reaction mechanism features a 2° radical, which captures O_2. This generates the key Co(III)peroxy species, which is reduced by the silane. Notably, the authors were able to obtain silylperoxy species using Ph_2SiH_2 or Et_2SiH_2.

Review: S. W. M. Crossley, C. Obradors, R. M. Martinez, R. A. Shenvi *Chem. Rev.* **2016**, *116*, 8912–9000.

SYNFACTS Contributors: Mark Lautens, Austin D. Marchese
Synfacts 2022, 18(09), 1001 Published online: 18.08.2022
DOI: 10.1055/s-0041-1738682; **Reg-No.:** L10022SF