The Catalytic Kulinkovich Reaction

Selected examples:

1. EtMgBr (2 equiv)
   Ti(O-i-Pr)4 (5–10 mol%)
   Et2O, 18–20 °C, 1 h
2. 5% H2SO4 (aq), 5 °C

6 examples
up to 95% yield

Proposed mechanism:

Significance: The Kulinkovich reaction generates cyclopropanols from simple Grignard reagents and esters in the presence of a titanium(IV) alkoxide catalyst. This reaction has been subsequently expanded to a wide range of substrates (see Review below) and an asymmetric version was also demonstrated by the group of Corey (J. Am. Chem. Soc. 1994, 116, 9345).

Comment: Although the group of Kulinkovich previously reported the synthesis of cyclopropanols through a titanium(IV) alkoxide mediated reaction (Zh. Org. Khim. 1989, 25, 2244), the current report demonstrated a method that was catalytic in titanium.