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Titanium(IV) Isopropoxide-Catalyzed Formation of 1-Substituted Cyclopropanols in the Reaction of Ethylmagnesium Bromide with Methyl Alkanecarboxylates


**The Catalytic Kulinkovich Reaction**

1. **EtMgBr (2 equiv)**
   
   2. **Ti(Oi-Pr)₄ (5–10 mol%)**
   
   **Et₂O, 18–20 °C, 1 h**

   6 examples up to 95% yield

**Selected examples:**

- **OH**
  - 76% yield

- **Et**
  - 79% yield

- **n-Pr**
  - 91% yield

- **n-Bu**
  - 90% yield

- **n-Pent**
  - 94% yield

- **n-C₉H₂₀**
  - 95% yield

**Proposed mechanism:**

- **2 EtMgBr**
- **2 J-PROMgBr**

**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.


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