The Kulinkovich Reaction

**Significance:** In 1991, Kulinkovich and co-workers reported the titanium-catalyzed reaction of simple esters with ethylmagnesium bromide, leading to substituted cyclopropanols in excellent yields.

**Comment:** Interestingly, in the presence of the titanium catalyst, ethylmagnesium bromide is transformed into an ethylene dianion, which is reactive towards alkylcarboxylic esters.

**Examples:**

<table>
<thead>
<tr>
<th>R = Alk</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>76%</td>
</tr>
<tr>
<td>n-PrOH</td>
<td>91%</td>
</tr>
<tr>
<td>n-C5H11OH</td>
<td>94%</td>
</tr>
<tr>
<td>n-C9H19OH</td>
<td>94%</td>
</tr>
</tbody>
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**Reaction mechanism:**

1. EtMgBr (2.0 equiv) Ti(Oi-Pr)4 (5–10 mol%) Et2O, 18–20 °C, 1 h
2. 5% aq H2SO4

1. EtOMgBr
2. 2 EtMgBr

1. Ti(Oi-Pr)4
2. (Oi-Pr)2Ti
3. (Oi-Pr)2Ti

1. C2H6
2. RCO2Me

1. R OH
2. H2O, H+