**1,4-Acetoxychlorination of Dienes: The Bäckvall Reaction**

**Significance:** Bäckvall and co-workers reported the regioselective 1,4-acetoxychlorination of 1,3-dienes using palladium catalysis under mild oxidative conditions. While cyclic dienes reacted with a lower palladium loading and with high stereoselectivity for the cis-isomer, large R² or R³ substituents increased the amount of (Z)-isomer for acyclic dienes. The stereospecific nature of the reaction was shown using two isomers of the same diene (E,E and E,Z) to give the syn- and anti-diastereomers, respectively, with high selectivity.

**Comment:** Synthetic utility was demonstrated by reaction of the product with nucleophiles under metal-catalyzed or SN2 conditions, to give products with retention or inversion of stereochemistry, respectively. Through investigation of reaction rates, a first-order dependence of p-benzoquinone (BQ) was observed, suggesting the coordination of BQ to palladium facilitates the external trans-attack by chloride. The authors proposed that the regioselectivity of the reaction was governed by thermodynamic considerations.

**Proposed mechanism:**

- **LiOAc•2H₂O (2 equiv)**
- **LiCl (2 equiv), AcOH, r.t.**
- **Pd(OAc)₂ (5 or 7.5 mol%)**
- **p-benzoquinone (2 equiv)**

**Selected examples:**

- 81% yield, E/Z = 9:1
- 44% yield, E/Z = 1:10
- 62% yield, >95% de
- >99% E from (E,Z)
- 55% yield, >98% de
- 58% yield, >95% de

**Further transformations:**

- **NaCH(CO₂Me)₂ (1.2 equiv)**
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- **Pd(OAc)₂ (2 mol%)**
  - **NaCH(CO₂Me)₂ (1.2 equiv)**
  - **NaCH(CO₂Me)₂ (1.2 equiv)**
  - **NaCH(CO₂Me)₂ (1.2 equiv)**

- **MeCN, reflux**
- **Ph₃P (10 mol%), THF, r.t.**
- **94% yield, >98% de**
- **95% yield, >98% de**