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.