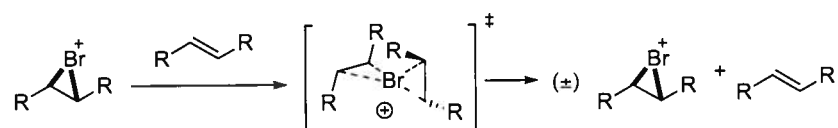


Studies on the Stereochemical Stability of Halonium Ions

Matthew T. Burk, Andrew Hoover, and Scott E. Denmark

Electrophilic halogenation of olefins is one of the simplest organic transformations, yet the stereochemical stability of the intermediate halonium ions remains underexplored, despite recent interest in enantioselective variants.

The absolute stereochemical integrity of bromonium and chloronium ions, and their enantiospecific trapping with several nucleophiles, has been demonstrated in the absence of added olefin. In the presence of added olefin, rapid racemization of bromonium ions via a degenerate exchange mechanism has been demonstrated. Chloronium ions do not racemize under the same conditions.



Palladium-Catalyzed Amination of Aromatic C-H Bonds Using Hydroxylamine Derivatives

Yichen Tan and John F. Hartwig

A new method for amination of aromatic C-H bonds under external-oxidant-free conditions has been developed. The cyclization of oxime acetate derived from arylketones provides indole products (51-71% yield) via amination of aromatic C-H bond. Pd(dba)₂ is used as catalyst and the presence of Cs₂CO₃ allows for the catalyst loading to be lowered to 1 mol % without a decrease in yield. Preliminary mechanistic study shows that this amination process is initiated by an irreversible N-O bond oxidative addition to the Pd(0).

