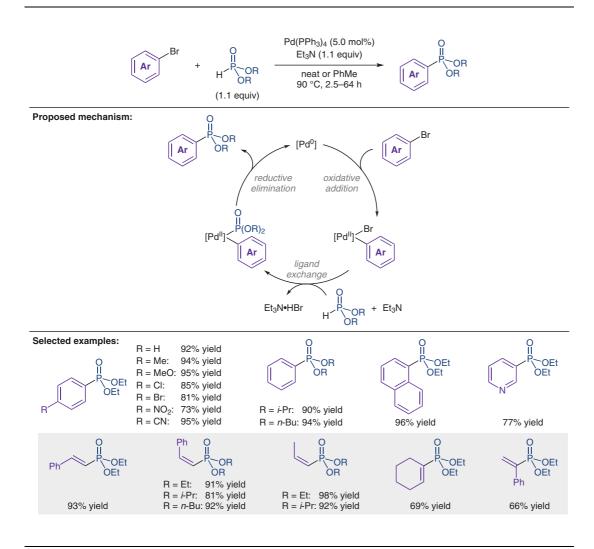
T. HIRAO*, T. MASUNAGA, Y. OHSHIRO, T. AGAWA (OSAKA UNIVERSITY, JAPAN) A Novel Synthesis of Dialkyl Arenephosphonates

Synthesis 1981, 56-57, DOI: 10.1055/s-1981-29335.

The Hirao Reaction: Palladium-Catalyzed Cross-**Coupling of Dialkyl Phosphites with Aryl Halides**



Significance: In 1981, Hirao and co-workers disclosed the direct cross-coupling of aryl halides with dialkyl phosphites in the presence of a palladium(0) catalyst and an amine base to give the corresponding aryl phosphonates. In contrast to the Michaelis-Arbuzov reaction, this protocol enables the facile formation of $C(sp^2)$ –P bonds.

Comment: While most products were isolated in good to excellent yields, the cross-couplings of para-hydroxyphenyl and para-aminophenyl halides were ineffective. The substrate scope was successfully extended to vinyl halides (Tetrahedron Lett. 1980, 21, 3595), affording the corresponding vinyl phosphonates in high yields (see grey box).

Category

Metals in Synthesis

Key words

C(sp²)–P bond formation

palladium catalysis

phosphonates

