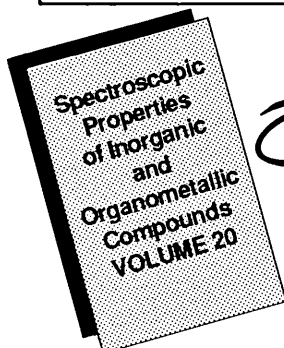


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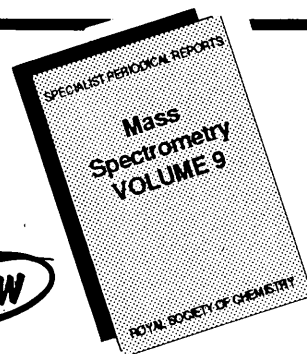
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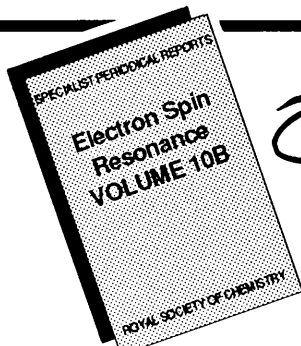
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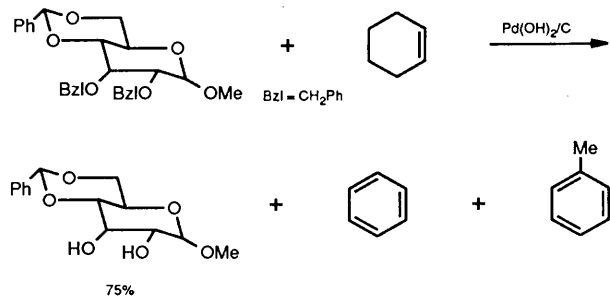


Organopalladium Chemistry

Palladium-assisted organic synthesis has developed rapidly in the past several years, and is the subject of several recent reviews.¹ Palladium complexes allow chemists increasing control of regiochemistry and stereochemistry in synthetic transformations. A wide variety of palladium complexes in both zerovalent and divalent states has found use in catalytic and stoichiometric applications including coupling reactions, allylic functionalization and molecular rearrangements. In addition to these homogeneous systems, palladium species dispersed on inert supports continue to find use in heterogeneous hydrogenation and hydrogenolysis reactions. Below is a survey of some recent synthetic applications of palladium.

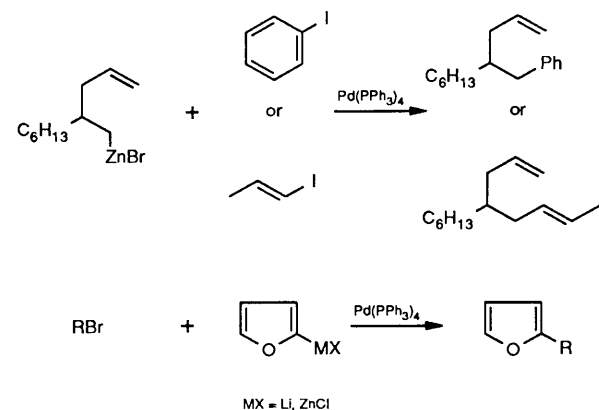
Cleavage of Benzyl Ethers

Palladium hydroxide on carbon (Pearlman's catalyst) cleaves benzyl ethers to toluene and an alcohol, using cyclohexene as the hydrogen source.² This hydrogenolysis is selective for the cleavage of benzyl ethers even in the presence of a benzylidene moiety.

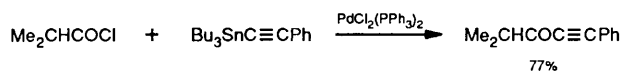


Coupling Reactions

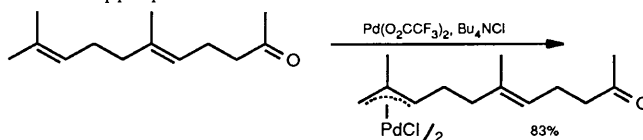
The coupling of aryl and alkenyl iodides with organozinc compounds,³ as well as the preparation of 2-substituted furans from organobromides and 2-metallo precursors,⁴ is catalyzed by **tetrakis(triphenylphosphine)palladium(0)**.



Palladium(II) catalysts are favored for the coupling of alkenyltin alkyls with acid chlorides.⁵

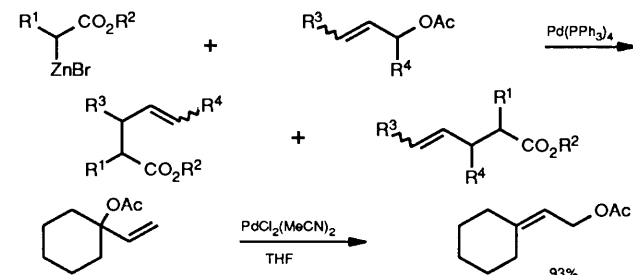


π -Allylpalladium complexes used for stoichiometric coupling reactions are readily prepared from **palladium trifluoroacetate** and the appropriate alkene.⁶

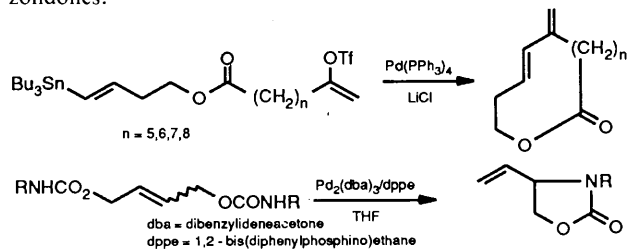


Allylic Functionalization and Rearrangement

Allylic acetates react with several palladium species, and the resulting π -allylpalladium system can undergo nucleophilic attack⁷ or 1,3-shifts.⁸



Palladium-catalyzed intramolecular cyclization has been used recently to prepare large-ring lactams⁹ and 4-vinyl-2-oxazolidones.¹⁰



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