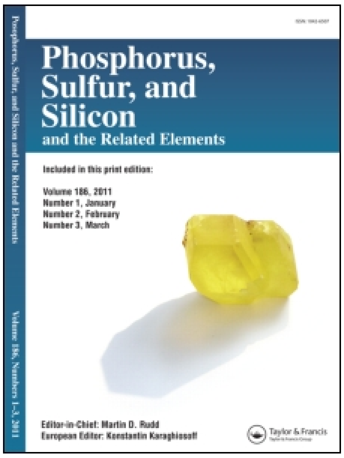

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The First Synthesis of α-Methylene Isophosphindoline Oxide

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The First Synthesis of α-Methylene Isophosphindoline Oxide

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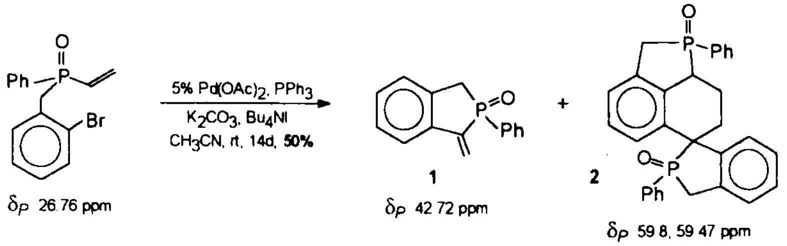
Over the last decade the intramolecular palladium-catalyzed coupling of haloarenes and haloalkenes with alkenes has proven to be a particularly valuable route to a wide variety of the structurally demanding cyclic and polycyclic systems. We wish now to demonstrate its successful application to the synthesis of the first parent representative of the five-membered ring carbon-phosphorus heterocycles possessing exocyclic unsaturation, a class of compounds remaining to date practically unexplored. The effected synthesis of the α-methylene isophosphindoline oxide **1** is delineated in the equation which reveals also the optimized catalytic system and the prerequisite reaction conditions. Of those, the reaction temperature is the most crucial parameter as the desired product undergoes unexpectedly facile thermal cyclodimerization to the spiropolycyclic system **2** frequently even precluding the isolation of **1**.



The regio- and stereoselectivity of the cyclodimerization of **1** have been determined on the basis of the X-ray analysis of **2**. Oxide **1** has also been tested in model hydrogenation and addition reactions.