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PALLADIUM CATALYZED CROSS-COUPLING REACTIONS OF ALKENYL (PHENYL) IODONIUM SALTS WITH ORGANOTIN COMPOUNDS

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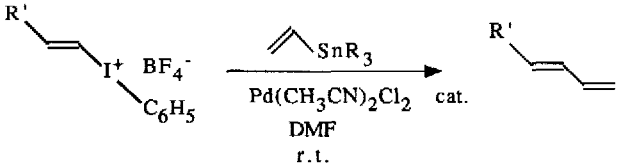
Abstract : Alkenyl (phenyl) iodonium salts undergo cross-coupling with both vinyl and allyl trialkyltin compounds stereoselectively and at room temperature. Mild conditions are attributed to the high reactivity of Pd (0) toward the electrophilic hypervalent iodine molecule .

The reactivity of hypervalent iodine compounds[1] in the presence of transition metal catalysts[2] has not been studied systematically. Previously, we reported that alkenyl (phenyl) iodonium compounds undergo palladium catalyzed coupling with with olefins stereoselectively, (again) at room temperature in a short period of time.[3] This indicated the ready formation of an alkenyl-palladium (II) intermediate as the initial step of the reaction. We now report the palladium catalyzed cross-coupling reactions of alkenyl phenyl iodonium salts with organotin compounds.[4]



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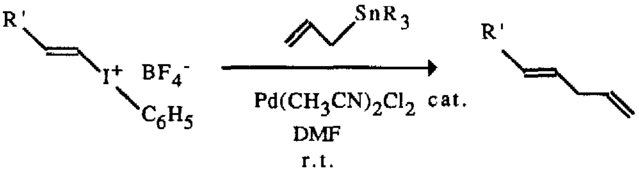
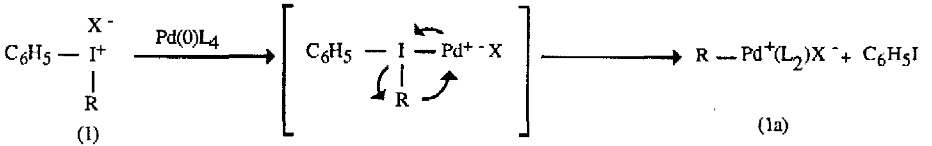


— (2)

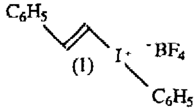
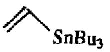
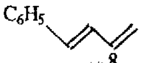
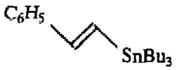
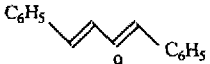
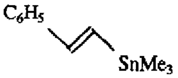
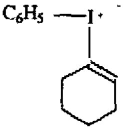
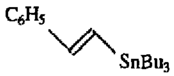
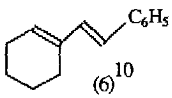
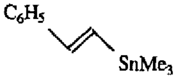
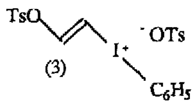
The reaction of alkenyl phenyl iodonium salts with alkenyl and allyl trialkyltin compounds with 5 mol% of $Pd(CH_3CN)_2Cl_2$ as the palladium catalyst yielded the corresponding 1,3 and 1,4 dienes in moderate to good yields stereoselectively at room temperature. As the alkenyl iodonium reagents, (2-phenylvinyl) phenyl iodonium tetrafluoroborate (1),[2b] 1-cyclohexenyl (phenyl) iodonium tetrafluoroborate 2[2b] and 2-tosyloxy-1-ethenyl (phenyl) iodonium tosylate (3)[3,5] were used. As the organotin compounds, vinyl tributyltin, allyl tributyltin, β-tributylstannyl styrene and β-trimethylstannyl styrene were used. Reaction times, especially with vinyl triorganotin reagents were short. Compared to the coupling reactions of alkenyl iodonium salts with olefins,[3] for the cross-coupling reactions with vinyl trialkyltin compounds the yields were lower and also were not as clean (though there were no other identifiable side products).[12] But the reactions with allyl tributyltin were clean, yields in general were higher, and it is significant to note that coupling reactions proceeded again at room temperature.



(3)

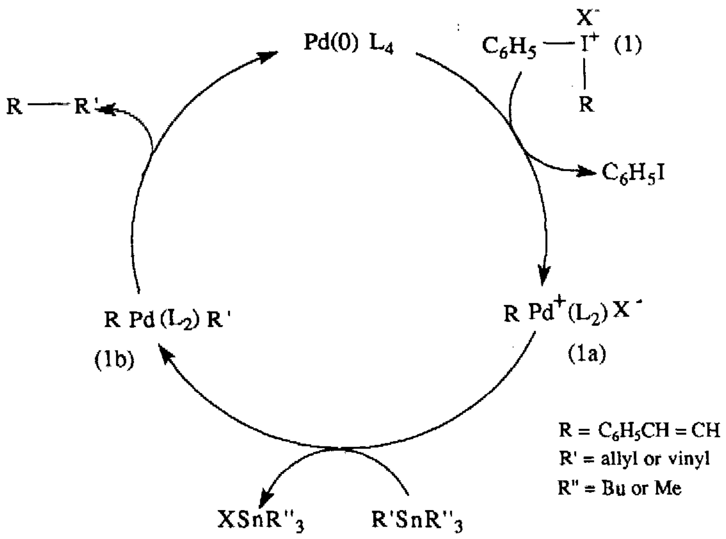
Table I

Palladium catalyzed cross-coupling of alkenyl iodonium salts with organotin compounds

Alkenyl Phenyl Iodonium Salt	Organotin Compound	Time	Product[a]	Yield[b] %
 (1)		5 min.	 (4)[8]	79
(1)		1 hr.	 (5)[9]	69
(1)		10 min.	(5)	53
 (2)		1 hr.	 (6)[10]	63
(2)		15 min.	(6)	63
(1)		5 hrs.	 (7)[11]	72
 (3)		5 hrs.	 (8)	80

(a) All products were characterized using ^{1}H, ^{13}C NMR, IR and Mass (CI +) spectroscopy.

(b) Isolated yield after chromatography[7].



Scheme 1

Mechanistically the significant step is the initial formation of an alkenyl-palladium(II) intermediate (1a, Equation 3). Formation of 1a could result from the initial reaction of Pd (0) with the electrophilic alkenyl iodonium (however generation of the intermediate through a transmetallation between I(III) and Pd(II) cannot be ruled out[3,6]). Reductive elimination of iodobenzene immediately afterwards would generate the intermediate 1a (Equation 3), which could go through the known mechanistic cycle illustrated in Scheme 1. The initial formation of the alkenyl-palladium(II) intermediate could also be considered as an oxidation of palladium (0) to palladium (II) by iodine (III) → iodine (I). If Pd (0) is considered as the catalytic species, facile reactivity of Pd(0) with the highly electrophilic hypervalent iodine atom as compared to the oxidative addition of Pd(0) to carbon-halide bond in an alkenyl halide could explain the mild conditions. Such an observation is not unprecedented. For example, alkenyl phenyl iodonium salts are more reactive towards nucleophilic substitution reactions as well. This has been attributed by Ochiai et al.[2b] to the higher leaving group ability of iodine (III) species.

In conclusion, we find that alkenyl phenyl iodonium salts readily undergo palladium catalyzed cross-coupling reactions with allyl and alkenyl triorganotin compounds. These reactions take place under mild conditions, consistent with our earlier observations.[3] The mild conditions could be due to the more facile reaction of Pd(0) with hypervalent iodine and this shows the potential of using hypervalent iodine for reactions where Pd (0) oxidative additions are too slow or require harsh conditions.

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7) In a typical reaction, to a stirred mixture of the alkenyl (phenyl) iodonium salt (0.5 mmol) and $Pd(CH_3CN)_2Cl_2$ (0.025 mmol, 5 mol%) in DMF (2 mL), under an Ar atmosphere, the organotin compound (1 mmol) was added and stirred for the time period given in Table I. The reaction was quenched by pouring it in to a solution of saturated aqueous NH_4Cl in a seperatory funnel. Extraction with EtOAc (x2), washing the combined extracts with saturated aqueous NH4Cl (x3), drying with anhydrous Na_2SO_4 followed by flash chromatography (silica gel, gradient elution, hexanes / EtOAc) yielded the pure product [characterized through IR, ^1H, ^{13}C NMR and mass (CI+) spectroscopy] in the yields mentioned in Table I.

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