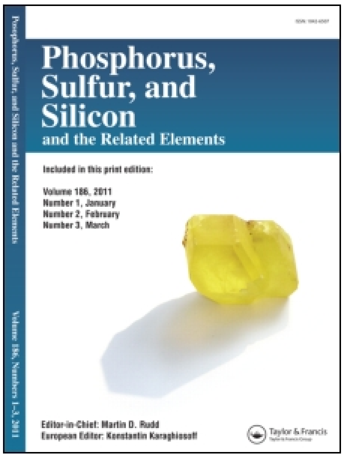

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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Organophosphorus Transition Metal Chemistry: Palladium Catalyzed Arylation of Tetra- and Tricoordinated Phosphorus Compounds

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To cite this Article Pietrusiewicz, K. M. and Kuźnikowski, M.(1993) 'Organophosphorus Transition Metal Chemistry: Palladium Catalyzed Arylation of Tetra- and Tricoordinated Phosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 77: 1, 57 — 60

To link to this Article: DOI: 10.1080/10426509308045618

URL: http://dx.doi.org/10.1080/10426509308045618

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, pp. 57–60
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ORGANOPHOSPHORUS TRANSITION METAL CHEMISTRY: PALLADIUM CATALYZED ARYLATION OF TETRA- AND TRICOORDINATED PHOSPHORUS COMPOUNDS

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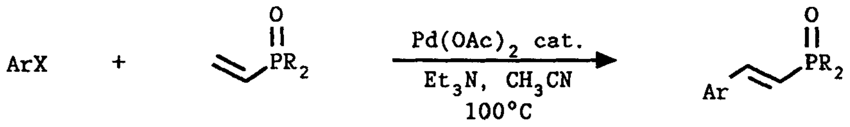
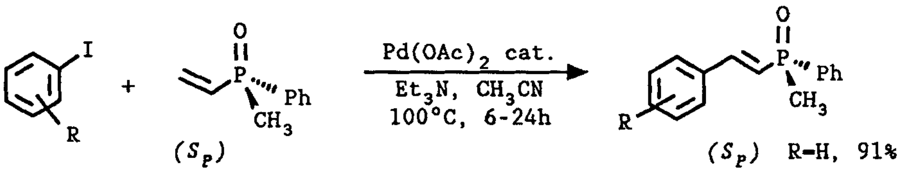
Abstract: A large variety of usefully functionalized α,β-unsaturated phosphine oxides (including bifunctional and homochiral ones), functionalized tetraaryl phosphonium salts and the C-P heterocyclic systems can be obtained directly by means of the Pd - catalyzed arylation of vinyl phosphine oxides, arylation of tertiary phosphines and aryl exchange processes in quaternary phosphonium salts.

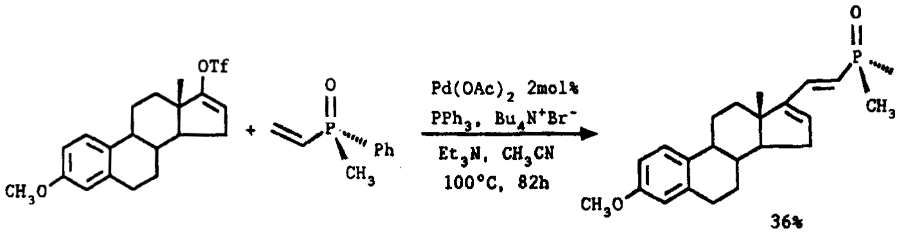
Several well established synthetic methodologies in organic chemistry are based on reactions utilizing catalytically derived aryl- and vinylpalladium reagents for carbon-carbon bond formation.[1] In organophosphorus chemistry the major use of these reagents has been to effect carbon-phosphorus bond formation.[2] In this report are presented our results on the use of some palladium catalyzed carbon-carbon and carbon-phosphorus bond forming processes for novel structural elaboration of organophosphorus compounds.



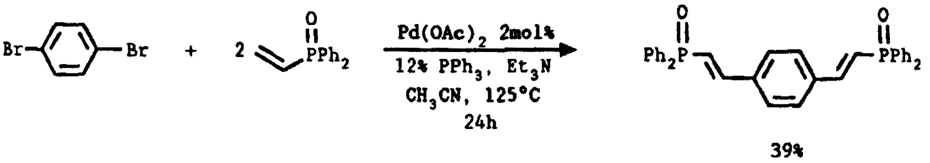
As shown in a general equation above phosphinylethenes readily undergo terminal arylations upon treatment with aryl iodides or aryl bromides under typical Heck reaction[3] conditions to afford the corresponding styrylphosphine oxides of E configuration. The reaction is very broad in scope in respect to both of the reaction components[4] and, importantly, can also be performed on a P-chiral phosphinylethene with full preservation of configurational integrity at P.



Analogous employment of vinylpalladium reagents leads to production of P-chiral phosphinylbutadienes in equally straightforward manner. An added feature of these vinylation reactions is that the relatively readily available chiral reagents can be used in combination with racemic phosphinylethenes and, therefore, a possibility for resolution of the P-stereogenic centre in the product can be simultaneously secured.

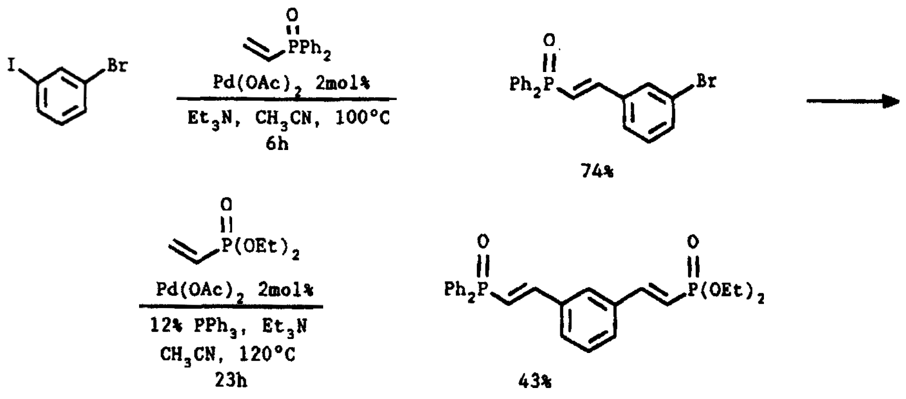


Bifunctional arylating agents in their reactions with two equivalents of phosphinylethene can readily afford diphosphinyl systems



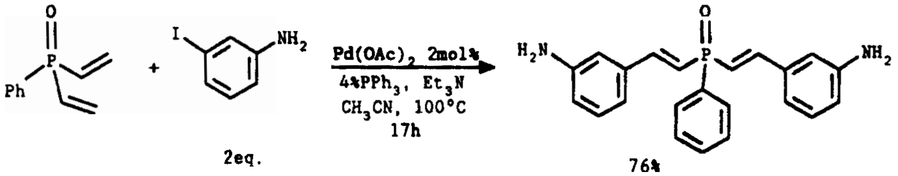
possessing the phosphinyl groups in either distal (shown) or proximal positions.

Advantage can also be taken of the known difference in reactivity of aryl iodides vs. aryl bromides in such reactions.[5] As exemplified in the equation below bifunctional systems possessing two different phosphorus functions can be readily synthesized in good overall yield.



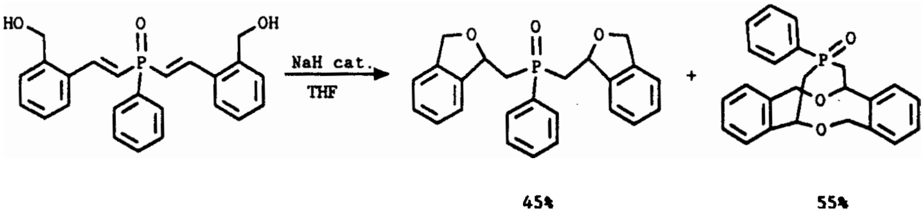
Moreover, by the possible sequential use of one homochiral and one racemic phosphinylethene in reactions of this type, systems in which one phosphorus centre would serve to resolve another can be created with facility.

Another useful facet of the studied reactions is connected with a possibility of using bifunctional organophosphorus substrates. As delineated below, use of divinylphenylphosphine oxide in combination



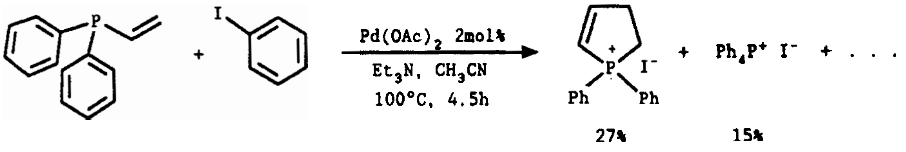
with 2 equivalents of aryl iodide leads expeditiously to the bifunctional styryl system which is suitably functionalized for further linear elaboration, or can be used as precursor to products of macrocyclic or polymeric nature.

Furthermore, proper placement of suitable functional groups in such systems may also open additional possibilities for intramolecular reactions. In the example cited below, upon treatment of bis(hydroxymethyl) derivative with catalytic amounts of NaH, a mixture of isomeric

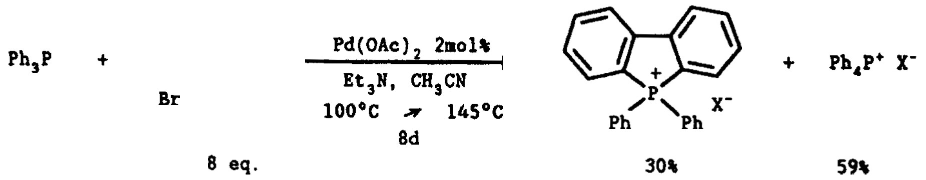


heterocycles resulting from both the "normal" and the interesting "crisscross" intramolecular addition reactions, has been obtained.

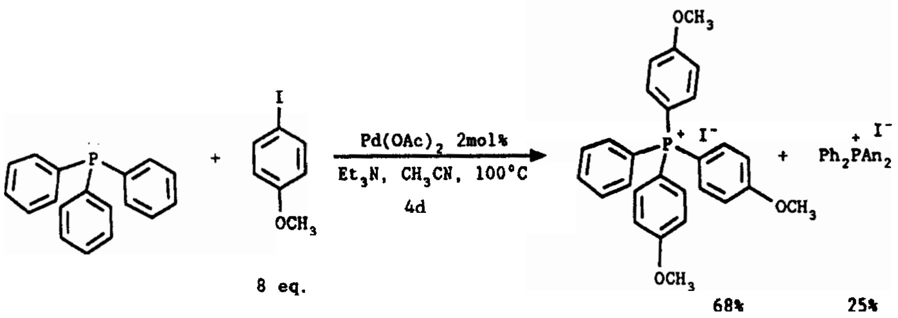
Another fruitful domain of interactions of arylpalladium reagents with organophosphorus compounds has been connected with the known Pd-catalyzed quaternization of tertiary phosphines by treatment with aryl halides.[2a] As we demonstrate in the following equations, again judicious placement of suitable functionalities in either of the



reaction components leads to attractive secondary transformations resulting in both cases in the formation of C-P heterocyclic products.



Moreover, we have been able to prove that under Pd-catalysis condition the aryl groups in tetraarylphosphonium salt can undergo aryl exchange with aryl iodides. In such a process tetraphenylphosphonium iodide (or Ph_3P, as shown below), upon exposure to an excess of iodoanisole can be converted into tris(*p*-anisyl)phosphonium iodide in very practical yields.



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