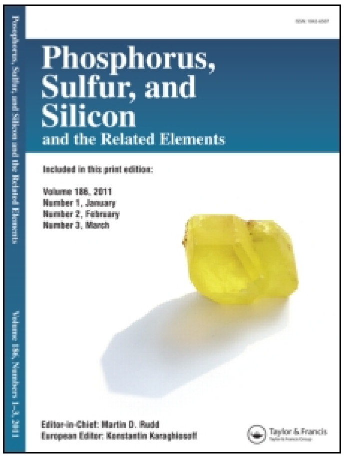

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of α-Aminophosphonic Acids Sy Pd(0)Alkylation of Diethyl Aminomethylphosphonate Schiff Bases

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To cite this Article Genet, J. P. , Uziel, J. and Juge, S.(1990) 'Synthesis of α-Aminophosphonic Acids Sy Pd(0)Alkylation of Diethyl Aminomethylphosphonate Schiff Bases', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 413
To link to this Article: DOI: 10.1080/10426509008040940
URL: http://dx.doi.org/10.1080/10426509008040940

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 413
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SYNTHESIS OF α-AMINOPHOSPHONIC ACIDS BY Pd(O)ALKYLATION OF DIETHYL AMINOMETHYLPHOSPHONATE SCHIFF BASES

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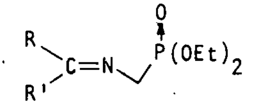
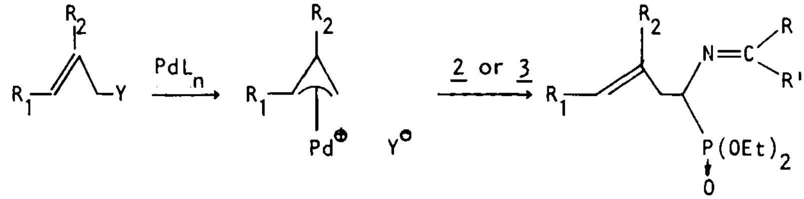
Aminoalkyl phosphonic compounds have many interesting biological properties: they are used as herbicides, antibiotics and enzyme inhibitors. Several approaches to the preparation of α-aminophosphonic acids have been reported. One efficient method using the schiff base of diethyl amino methylphosphonate 1 has been developped, allowing alkylation at the α carbon after deprotonation using strong bases such as LDA. In our continuing program dealing with the synthesis of unusual α-aminoacids which relies on C-C bond formation by transition metal catalyzed reactions (1), we report here a method based on the palladium-promoted alkylation of diethyl aminophosphonate schiff bases 2 and 3 with η^3-allyl species 5 generated *in situ* from the allylic derivative 4:

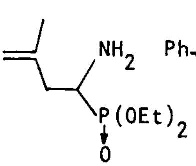


1 R=H R'=Ph 2 R=H R'=pPhCl
3 R = R' = Ph

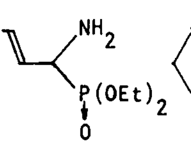


4 Y = OAc, Cl, OCO_2Et... 5 6

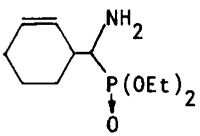
The schiff bases 2, 3 as their lithium or sodium enolates react with allylic esters in the presence of catalytic amounts of PdL$_n$: the most efficient catalyst is the preformed Pd(dppe)$_2$ or this generates *in situ* from Pd(dba)$_2$ or Pd(OAc)$_2$ by adding 2 equiv. of DPPE. The α-alkylated products 6 can be readily hydrolyzed (HCl, 4 equiv., 24 h, r.t) into the corresponding α-alkylated α-aminophosphonic esters 7-11 in 62-84% yields. For instance, we have prepared the phosphonic analogues 8 and 11 which are enzymes inhibitors.



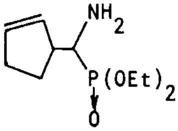
7 (67% yield)



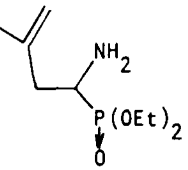
8 (81%)



9 (80%)



10 (62%)



11 (84%)

1) J.P.Genêt, S.Juge, S.Achi, S.Mallart, J.Ruiz-Montès and G.Levif Tetrahedron, 1988, 44, 5263 and references cited therein.