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Synthesis of Vinyldiphenylphosphines by Pd-Catalyzed Cross-Coupling Reactions of Diphenylphosphine with Alkenylhalides.

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Abstract: α- and β-alkoxy (α- and β-dialkylamino)vinylphosphines were synthesized by palladium catalyzed reactions of the corresponding vinylhalides with diphenylphosphine or diphenyltrimethylsilylphosphine in high yields. © 1998 Elsevier Science Ltd. All rights reserved.

Alkenylphosphines including functionalized derivatives are useful as ligands for transition metals.[1] However their use is limited in comparison with arylphosphines because they are less stable and less readily available. Standard syntheses of vinylphosphines are the reaction of vinylmagnesium or lithium derivatives with halophosphines[2] and the addition of primary or secondary phosphines to alkynes.[3] The first method cannot be applied to the synthesis of vinylphosphines with functional groups and the second method usually gives mixtures of isomers.

Cross-coupling reactions are widely used for the creation of carbon-heteroatom bonds, such as C-S,[4] C-N,[5] C-P[6] and so on,[7] including arylphosphines. The reactions of diphenyltrimethylsilylphosphine (Ph_2PSiMe_3) or diphenyltrimethylstannylphosphine (Ph_2PSnMe_3) with ArI are catalyzed by palladium complexes.[6a] Recently this reaction was performed using primary or secondary phosphines Ph_2PH or $PhPH_2$ and ArI[6e] or ArOTf,[6f] but this reaction has never been used for the synthesis of vinylphosphines.

Earlier, we described that 2-alkoxy- or 2-dialkylamino-2-halogenovinylphosphines can be obtained by the addition of halogenophosphines to electron-rich alkoxy- or dialkylaminoacetylenes.[8] The 2-alkoxyvinylphosphines, as we have shown, can be synthesized by the phosphination of enol ethers in the presence of tertiary amines.[9]

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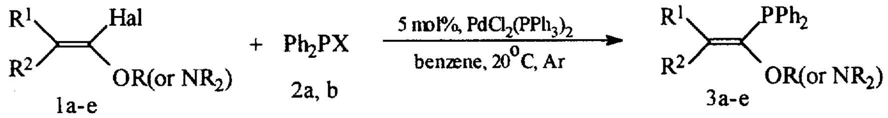
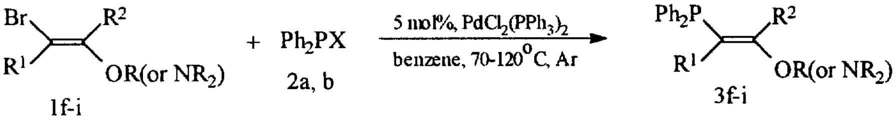
We report here the use of palladium-catalyzed cross-coupling reactions of diphenylphosphine and diphenyltrimethylsilylphosphine with functionalized vinylhalides. The results of our experiments are summarized in the Table.

The vinylation of diphenylphosphine by alkenyl halides (**1a-f**) was carried out in benzene using 5 mol% $PdCl_2(PPh_3)_2$ as a catalyst and Et_3N as a base.

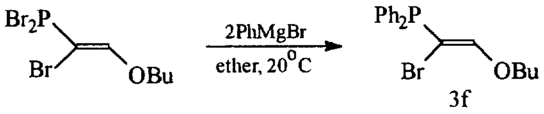
The carbon-halogen bond in vinylhalides (**1a-e**) is very reactive due to the effect of the α-alkoxy- or α-dialkylamino groups and these compounds react with diphenylphosphine Ph_2PH (**2a**) under mild conditions giving products in high yields (entries 1-5). The use of diphenyltrimethylsilylphosphine Ph_2PSiMe_3 (**2b**) in these reactions allows the pure product to be obtained without additional purification, but needs a prolonged time for completion (entries 1,2,4,5).



Alkylvinyl ethers having a bromine atom in the β-position are much less reactive than their α-isomer and 2,2-dibromovinylbutyl ether (**1f**) needs high temperature for reaction with diphenylphosphine Ph_2PH and diphenyltrimethylsilylphosphine Ph_2PSiMe_3 (entry 6) but gives the product with a practically quantative yield.



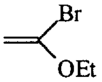
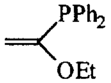
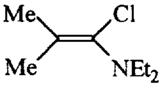
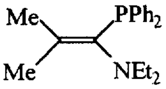
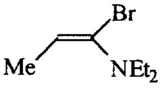
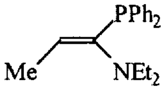
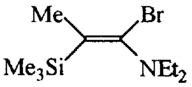
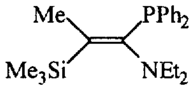
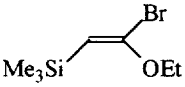
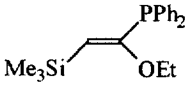
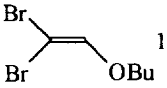
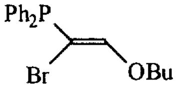
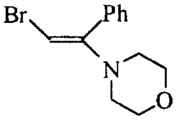
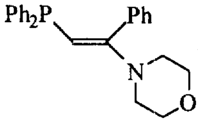
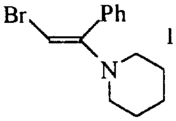
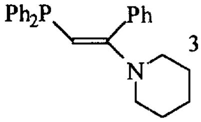
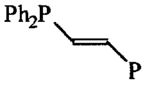
The 2,2-dibromovinylbutyl ether reacts with diphenylphosphine to give the *E*-isomer, which on keeping or distillation undergoes interconversion into its *Z*-isomer (**3f**).[10] The structure of phosphine (**3f**) was confirmed by its synthesis from (1-bromo-2-butoxyvinyl)dibromophosphine[9].



2-Bromoenamines (**1g, h**) react with diphenylphosphine Ph_2PH and diphenyltrimethylsilylphosphine Ph_2PSiMe_3 at 70°C and the reaction with diphenylphosphine Ph_2PH gives a very high yield of product (entries 7,8). However with less reactive diphenyltrimethylsilylphosphine Ph_2PSiMe_3 the reaction needs 45-50h for completion and because the starting compounds are not very stable the yields are rather modest (entries 7,8).

E-Bromostyrene reacts with Ph_2PH with net retention of configuration (entry 9).

TABLE Phosphination of vinylhalides

Entry	Vinylhalide	Alkenylphosphine	Method[a]	Temp (°C)/ Time (h)	Yield[b], %
1	 1a	 3a	A B	20 / 1 20 / 1.5	97 92
2	 1b	 3b	A B	20 / 6 20 / 12	84 80
3	 1c	 3c	A[c]	20 / 5	70
4	 1d	 3d	B[c]	20 / 12	70
5	 1e	 3e	B[c]	20 / 70	80
6	 1f	 3f	A B	120 / 36 120 / 40	94 90
7	 1g	 3g	A B	70 / 24 70 / 50	92 60
8	 1h	 3h	A B	70 / 24 70 / 45	90 55
9	 1i	 3i	A	100 / 6	90

[a] Method A: Ph_2PH (2a), 5mol% $PdCl_2(PPh_3)_2$, Et_3N, benzene under Ar; method B: Ph_2PSiMe_3 (2b), 5mol% $PdCl_2(PPh_3)_2$, benzene under Ar; [b] All compounds gave satisfactory ^1H, ^{31}P, ^{13}C NMR, IR and microanalysis; [c] Starting vinyl halides were synthesized *in situ*.

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REFERENCES.

1. (a) Fryzuk M.D.; Gao X.; Rettig S.J. *Can. J. Chem.* **1985**, *73*, 1175; (b) Weber L.; Kaminski O.; Boese R.; Blaser D. *Organometallics*, **1995**, *14*, 820; (c) Soulivong D.; Wieser C.; Marcellin M.; Matt D.; Harriman A.; Toupet L. *J. Chem. Soc., Dalton Trans.* **1997**, 2257.
2. *Organic Phosphorus Compounds*; 2nd ed.; Kosolapoff G. M.; Maier L.,Eds.; Wiley Interscience: New-York, 1972; vol.1.
3. Wolfsberger, W.; *Chem. Zeitung,* **1988**, *112*, 53.
4. (a) Migita, T.; Shimizu, T.; Asami, Y.; Shibara, J.-I.; Kato, I.; Kasugi, M. *Bull. Soc. Chem. Jpn.* **1980**, *53*, 1385; (b) Murahashi, S.-I.; Yamamura, M.; Yanagesava, K.; Mita, M.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408; (c) Dickens, M. J.; Gilday, J. P.; Mowlem, T. J.; Widdowson, D. A. . *Tetrahedron*, **1991**, *47*, 8621; (d) Arnold J. C.; Didelot, M.; Cadilhak, C.; Pasquet, M. J. *Tetrahedron Lett.* **1996**, *37*, 4523.
5. (a) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, 116, 7901; (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1348; (c) Wolf, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133; (d) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969; (e) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217.
6. (a) Tunnay, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748; (b) Efimova, I. V.; Kazankova, M. A.; Beletskaya, I. P. *XII Int. Conf. on Phosphorus chem. 1992,* 1-67; (c) Veits, Yu. A.; Karlstedt, N. B.; Beletskaya, I. P. *Zh. Org. Khim.* **1994**, *30*, 66; (d) Cai, D.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *J. Org. Chem.* **1994**, *59*, 7180; (e) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, *522*, 69; (f) Gilbertson, S. R.; Starkey, G. V.; *J. Org. Chem.* **1996**, *61*, 2922.
7. Kosugi, M.; Ohya, T.; Migita, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3855.
8. (a) Kazankova, M. A.; Luzikova, E. V.; *Zh. Obsh. Khim.* **1996**, *66*, 1637; . (b) Kazankova, M. A.; Luzikova, E. V.; *Zh. Obsh. Khim.* **1996**, *66*, 1652.
9. Kazankova, M. A.; Trostyanskaya, I. G.; Efimova, I. V.; Beletskaya, I. P. *Zh. Org. Khim.* **1996**, *32*, 1657.
10. Spectral properties of *E*- and *Z*-isomers of **3f** are as follows: *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, 1H, J=22.0 Hz, =**CH**); ^{31}P NMR (C_6H_6, 32.2MHz): δ -15.51; *Z*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (d, 1H, J=8.9 Hz, =**CH**); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 73.46 (s, OCH_3), 97.88 (d, J=39.2 Hz, P-C=), 133.93 (d, J=18.5 Hz, *ipso*-C), 157.81 (d, J=72.9 Hz, =C-O); ^{31}P NMR (C_6H_6, 32.2MHz): δ -3.21.