Pergamon

Tetrahedron Letters 43 (2002) 5817–5819

TETRAHEDRON
LETTERS

t-BuOK-catalyzed addition phosphines to functionalized alkenes: a convenient synthesis of polyfunctional phosphine derivatives

Tanasri Bunlaksananusorn and Paul Knochel*

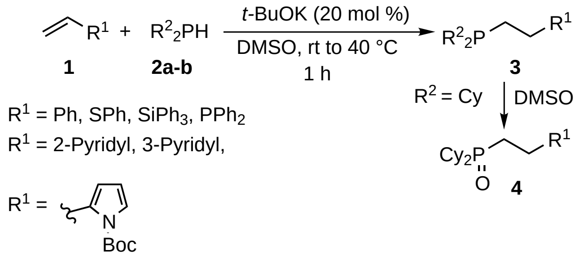
Ludwig-Maximilians-Universität München, Institut für Organische Chemie, Butenandtstrasse 5-13, Haus F, D-81377 München, Germany

Received 24 April 2002; revised 14 June 2002; accepted 17 June 2002

Abstract—The use of *t*-BuOK in DMSO allows a smooth addition of Ph_2PH, Cy_2PH and $Ph_2P(O)H$ to various functionalized alkenes leading to polyfunctional phosphines in good yields. This method has been used to prepare precursors for P,P- and P,N-ligands. © 2002 Elsevier Science Ltd. All rights reserved.

The preparation of functionalized phosphines is an important synthetic goal since these can act as ligands for many metallic salts used for the catalysis of organic reactions.[1] Recently, we have found that catalytic amounts of *t*-BuOK in *N*-methylpyrrolidinone (NMP) considerably facilitate the addition of various carbonyl compounds to styrenes[2] and other olefins bearing weakly activating groups like silyl, thio or phosphorus functions.[3] The addition of phosphines to alkenes has been studied and requires either radical initiation,[4] transition metal catalysis[5] or strong basic conditions.[6] The use of phosphine–borane complexes is also possible and allows selective hydrophosphination.[7]

Herein, we wish to report that catalytic amounts of *t*-BuOK (20 mol%) in DMSO allow the hydrophosphination of functionalized alkenes of type **1** using either diphenylphosphine (**2a**) or an aliphatic dialkylphosphine like dicyclohexylphosphine (**2b**), leading to functionalized phosphines of type **3** (Scheme 1 and Table 1). Thus, styrene (**1a**) reacts very fast with Ph_2PH (**2a**) (rt, 1 h), leading to **3a** in 83% yield (entry 1 of Table 1). Slightly activated alkenes like the vinylic thioether **1b**, the vinylic silane **1c** and the vinylic phosphine **1d** react under similar conditions, furnishing the polyfunctional phosphines **3b–d** (entries 2–4) in 80–90% yield. Heterocyclic compounds bearing a vinyl group also react with diphenylphosphine leading to potential P,N-ligands (**3e–g**; 63–68%, entries 5–7). Interestingly, whereas 2-vinylpyridine (**1e**), bearing an unsaturated vinylic imine unit was expected to react well, we have observed that the isomeric cross-conjugated 3-vinylpyridine (**1f**) reacts equally as fast (rt, 1 h, entry 6). Triethoxyvinylsilane (**1h**) reacts in the presence of EtOK (used instead of *t*-BuOK in order to avoid alkoxide scrambling), leading to the phosphine **3h**, which can be used to attach a phosphine unit on silica gel.[8] The reaction with Cy_2PH proceeds similarly. However its addition to styrene produces the phosphine oxide **4**. The sensitive intermediate dicyclohexylphosphine adduct is oxidized by DMSO leading to **4** in 73% yield (entry 9).



Scheme 1.

We found that these basic conditions also allow addition of the cyclic hydrogen phosphonate[9] **5** to styrene (**1a**), leading to the adduct **6** in 87% yield (Scheme 2). Attempts to add diphenylphosphine (**2a**) to trisubstituted unsaturated pyridines like **7** led to long reaction times and the mixtures of the phosphine oxide adduct **9** and the corresponding phosphine. However, diphenylphosphine oxide **8** reacts faster and affords only the product *trans*-**9** in 50% yield as a single

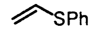
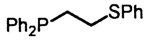
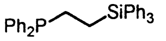
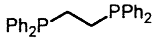
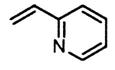
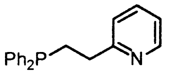
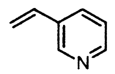
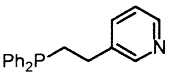
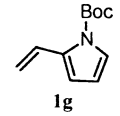
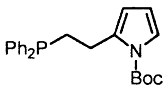
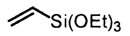
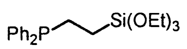
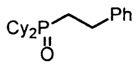
---

Keywords: addition reaction; phosphine ligands; diphosphines; functionalized phosphines.

* Corresponding author. Tel.: +49-89-2180-7679; fax: +49-89-2180-7680; e-mail: paul.knochel@cup.uni-muenchen.de

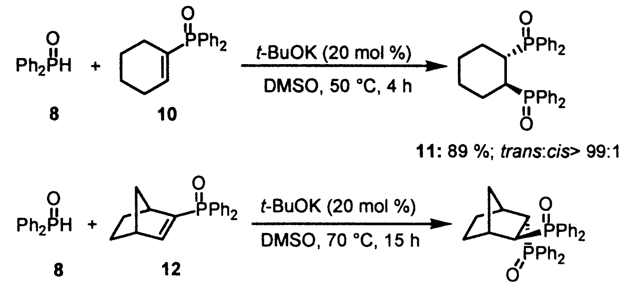
0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)01177-2

Table 1. Functionalized phosphines **3a**–**h** and phosphine oxide **4** obtained by the *t*-BuOK catalyzed addition of phosphines **2a**–**b** to functionalized alkenes **1a-h** in DMSO at rt

Entry	Alkenes **1**	Phosphines **2**	Product of type **3**	Yield (%)[a]
1	 **1a**	Ph_2PH **2a**	 **3a**	83
2	 **1b**	**2a**	 **3b**	80
3	 **1c**	**2a**	 **3c**	88[b]
4	 **1d**	**2a**	 **3d**	90
5	 **1e**	**2a**	 **3e**	63
6	 **1f**	**2a**	 **3f**	65
7	 **1g**	**2a**	 **3g**	68
8	 **1h**	**2a**	 **3h**	81[c]
9	 **1a**	Cy_2PH **2b**	 **4**	73

[a]Isolated yield of analytically pure products. [b]The reaction was performed at 40 °C. [c]EtOK (20 mol %) in NMP was used.

diastereoisomer[10] (Scheme 2). 1,2-Diphosphine oxides can be easily prepared by this method. Thus, the addition of **8** to the trisubstituted cyclohexenylphosphine oxide (**10**) leads to the C_2-symmetrical phosphine oxide **11**[11] in 89% yield (*trans*:*cis*>99:1). A similar addition of **8** to the phosphine oxide **12** furnishes the diphenylphosphine oxide of *rac*-renorphos[12] (**13**) in 69% yield (*trans*:*cis*>99:1) (Scheme 3).



11: 89 %; *trans*:*cis*> 99:1

13: 69 %; *trans*:*cis*> 99:1

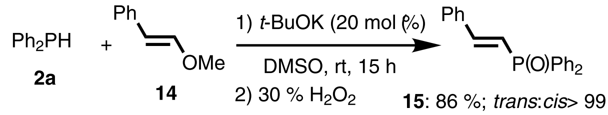
Scheme 3.

Finally, addition–elimination reactions are also possible. Remarkably, the reaction of Ph_2PH (**2a**) with β-methoxystyrene (**14**) leads to **15**, the product of the substitution of the methoxy groups by the diphenylphosphine oxide moiety in 86% yield uniquely as the *trans*-product.[13] We tentatively propose that this reaction occurs via an addition–elimination mechanism (Scheme 4).

In summary, we have developed a very convenient procedure for adding diphenylphosphine to a variety of functionalized alkenes under mild conditions. Applications to asymmetric catalysis are underway.[14]

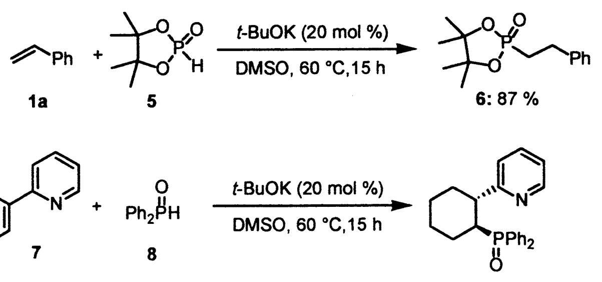
Acknowledgements

We thank the DFG (Leibniz-Program) and the Fonds der Chemischen Industrie for generous financial support. We thank Chemetall GmbH (Frankfurt), the Degussa AG (Hanau) and BASF AG for the generous gift of chemicals.



15: 86 %; *trans*:*cis*> 99:1

Scheme 4.



6: 87 %

9: 50 %; *trans*:*cis*> 99:1

Scheme 2.

References

1. (a) Hartley, F. R. In *The Chemistry of Organophosphorus Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1990; Vol. 1; (b) Quin, L. D. In *A Guide to Organophosphorus Chemistry*; John Wiley and Sons, 2000.
2. Rodriguez, A. L.; Bunlaksananusorn, T.; Knochel, P. *Org. Lett.* **2000**, *21*, 3285.
3. Bunlaksananusorn, T.; Rodriguez, A. L.; Knochel, P. *J. Chem. Soc., Chem. Commun.* **2001**, 745.
4. (a) Therrien, B.; König, A.; Ward, T. R. *Organometallics* **1999**, *18*, 1565; (b) Mitchell, T. N.; Heesche, K. *J. Organomet. Chem.* **1991**, *409*, 163; (c) Therrien, B.; Ward, T. R. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 405.
5. (a) Shulyupin, M. O.; Kazankova, M. A.; Beletskaya, I. P. *Org. Lett.* **2002**, *4*, 761; (b) Douglass, M. R.; Mark, T.J. *J. Am. Chem. Soc.* **2000**, *122*, 1824; (c) Takaki, K.; Takeda, M.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 6357.
6. (a) Knühl, G.; Sennhenn, P.; Helmchen, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1845; (b) Khachatryan, R. A.; Sayadyan, S. V.; Grigoryan, N. Y.; Indzhikyan, M. G. *Zh. Obshch. Khim.* **1988**, *58*, 2472; (c) Arbuzova, S. N.; Gusarova, N. K.; Malysheva, S. F.; Brandsma, L.; Albanov, A. I.; Trofimov, B. A. *Zh. Obshch. Khim.* **1996**, *66*, 56; (d) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 63; (e) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1971**, *93*, 4158.
7. (a) Bourumeau, K.; Gaumont, A.-C.; Denis, J.-M. *Tetrahedron Lett.* **1997**, *38*, 1923; (b) Bourumeau, K.; Gaumont, A.-C.; Denis, J.-M. *J. Organomet. Chem.* **1997**, *529*, 205.
8. Tsiavaliaris, G.; Haubrich, S.; Merckle, C.; Blümel, J. *Synlett* **2001**, *3*, 391.
9. Han, L.-B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407.
10. Demay, S. Ph.D. Thesis, Ludwig-Maximilians-Universität München, 2001.
11. Demay, S.; Volant, F.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1235.
12. Kyba, E. P.; Davis, R. E.; Juri, P. N.; Shirley, K. R. *Inorg. Chem.* **1981**, *20*, 3616.
13. ^{1}H NMR indicates that the *trans*-isomer is formed ($J_{trans} = 22$ Hz).
14. Typical procedure, preparation of 1-diphenylphosphino-2-phenylthioethane (**3b**): To a stirred solution of potassium *tert*-butoxide (45 mg, 0.4 mmol) in DMSO (2 mL) were successively added under argon, diphenylphosphine (**2a**; 370 mg, 2 mmol) and phenyl vinyl sulfide (**1b**; 270 mg, 2 mmol). The reaction was stirred at rt for 1 h. Water (5 mL) and CH_2Cl_2 (25 mL) were added, and the reaction mixture was quenched with brine (10 mL), dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash chromatography (2% ether in pentane), giving the desired product **3b** (217 mg, 80% yield).