Reduction of $R_3P=O$ to R_3P in $Mg/Me_3SiCl/DMI$ System

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Ph_3P is widely used in synthesis of natural products via Wittig reaction, Mitsunobu reaction, Mukaiyama-Corey lactonization, Appel reaction, Staudinger reaction, and so on. In these reactions, Ph_3P is oxidized to afford $Ph_3P=O$. From the view of atom economy strategy, recycle use of P compounds to use it repeatedly is a keen project.[1] For this purpose, a combination of reductant (P^V to P^{III}) and deoxygenizer should be developed. We chose Mg as a powerful and air-stable reductant, and Me_3SiCl as a deoxygenizer.[2]

We examined the reduction under several reaction conditions, and found that the solvent is the most important factor[3] for this reduction (Table 1). This reduction only proceeded in DMI (1,3-dimethylimidazolidinone) to give Ph_3P quantitatively (Entry 1): in other solvents such as MeCN, DMF, DMAc, NMP, DMPU, and THF, most of $Ph_3P=O$ was recovered intact Entries 2-7).

Several phosphine oxides were reduced under similar reaction conditions (Table 2). Triarylphosphine oxides gave the corresponding triarylphosphine in quantitative yields (entries 1–4), whereas triarylphosphine oxide having an electron-withdrawing group such as (4-cyanophenyl)diphenylphosphine oxide gave only a complex mixture (Entry 5). Alkyldiarylphosphine oxides (entries 6 and 7) and dialkylarylphosphine oxide (entry 8) were also reduced with the $Mg/Me_3SiCl/DMI$ system to afford the corresponding phosphine derivatives in good yields, whereas, trialkylphosphine oxide was not reduced at all (Entry 9).

In this stage, we have no critical answer why the reduction occurs only in DMI, since DMI itself is not a unique solvent.[4] However, (a combination of) solvent (and additive) sholud play an important role especially in Electron-Transfer Reaction. We would like to discuss such phenomena in the E-poster.

Table 1. Mg/Me_3SiCl Promoted Reduction of $Ph_3P=O$ to Ph_3P^a

Run	Solvent	Ph_3P^b	$Ph_3P=O^b$
1	DMI	98	1
2	MeCN	9	91
3	DMF	7	93
4	DMAc	n.d.	100
5	NMP	n.d.	100
6	DMPU	n.d.	100
7	THF	n.d.	100

[a]Conditions: $Ph_3P=O$ (2 mmol), Mg (6 mmol), Me_3SiCl (6 mmol), Solvent (8 mL), rt, 2 h. [b] ^{31}P NMR yield.

Table 2. Reduction of $R^1_2R^2P=O$ to $R^1_2R^2P$

Run	R^1	R^2	$R^1_2R^2P^a$	$R^1_2R^2P=O^a$
1	*o*-Tolyl	*o*-Tolyl	95	4
2	*m*-Tolyl	*m*-Tolyl	91	7
3	*p*-Tolyl	*p*-Tolyl	95	5
4	*p*-Anis	*p*-Anis	94	6
5	Ph	*p*-NCC_6H_4	comp	n.d.
6	Ph	Pr	37	22
7	Ph	Et	96	4
8	Et	Ph	35	57
9	Oct	Oct	n.d.	98

[a] ^{31}P NMR yield.

[1] *Tetrahedron* **2011**, *67*, 5825. *Synthesis* **2011**, 4094-4098. [2] *J. Fluorine Chem.* **2013**, *152*, 84-89. [3] The reduction did not proceed with Zn and Al. The reduction did not proceed without Me_3SiCl. [4] DMI itself is not so highly polar solvent since donor number (DN) and acceptor number (AN) of DMI (DN/AN 27/19) is similar to those of MeCN (14/20), DMF (29/21), and THF (20/8). However, DN and AN of DMI (62/52) and DMF (78/48) increased remarkably by addition of a small amount of $MgCl_2$ (0.1 M). The electron transfer from Mg to $R_3P=O$ would only occur in such highly polar environment.

Biography

KUROBOSHI (born in 1961) has completed his PhD at the age of 27 from Kyoto University and moved Sagami Chemical Research Center (27-30), Tokyo Institute of Technology (30-33), and Okayama University (33-now). He is now an associate professor in Okayama University. His main research interests are in electroorganic chemistry and heteroatom chemistry.

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