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Highly Efficient Reduction of Tertiary Phosphine Oxides and Sulfides with Amine-assisted Aluminum Hydrides under Mild Conditions[1]

Shuyan Yang, Xinxin Han, Minmin Luo, Jing Gao,
Wenxiang Chu, and Yuqiang Ding

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education,
School of Chemical and Material Engineering, Jiangnan University,
Wuxi 214122, Jiangsu Province, China
e-mail: yding@jiangnan.edu.cn

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Abstract—Reduction of tertiary phosphine oxides and sulfides into the corresponding phosphines with amine-assisted aluminum hydrides has been studied. The method is characterized by mild conditions, short reaction time, high efficiency, and expanded substrate scope. The new method is an alternative to the currently used methods of reducing phosphine oxides or recycling phosphines engaged in organic reactions.

Keywords: reduction reaction, amine-assisted, phosphides, aluminum hydrides

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INTRODUCTION

Phosphines and their derivatives represent an important class of compounds for life science and chemical industry [1–6] (Scheme 1). Reduction of phosphine chalcogenides has been a significant challenge in phosphorus chemistry.

Currently reduction of phosphine oxides [13–16], versus substitution reactions of carbon nucleophiles with P–Cl derivatives or of carbon electrophiles with alkali metal phosphides [7–9], and phosphination of alkenes, alkynes, or aromatic halids [10–12], is the major method of synthesis of phosphines. Among many reducing agents silanes and aluminum hydrides remain the reagents of choice for reduction of phosphine oxides [17–25].

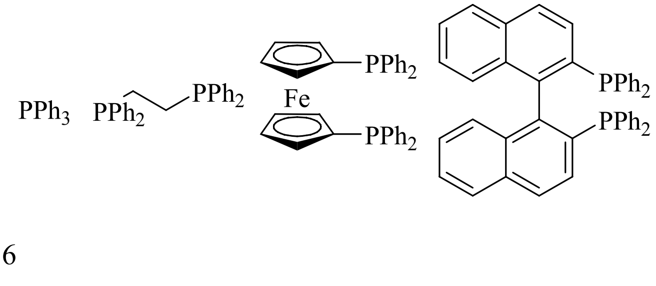
Herein we present reduction of phosphine oxides and sulfides by amine-assisted aluminum hydrides that needs no auxiliary catalysts and its advantages (Scheme 2).

RESULTS AND DISUSSION

The first step of the study was testing various sources of amine-assisted aluminum hydrides as hydride sources. Triphenyl phosphine oxide was considered as the model substrate. All tests were performed with 1 equiv. of aluminum hydrides at room temperature under the atmosphere of nitrogen with reaction time 10 min (Table 1). Amine-assisted aluminum hydrides in THF media gave excellent yields of products (Table 1, entries 1–3). Further optimization of the process was performed with the compound **Ic** used as the source of hydride in various solvents. According to the accumulated data the reaction was strongly solvent-dependent (Table 1, entries 4–10) and could not occur without the aluminum complex (Table 1, entry 11).

The process under study (Table 2) led to different phosphines with moderate to high yields upon the action of aluminum complex **Ic**. Generally, the reaction had high substituent tolerance. The aryl ring substituents with different electronic properties had little influence on the reaction yields. Similar conditions of the reaction were applied to bisphosphine

Scheme 1. Some important phosphine ligands.



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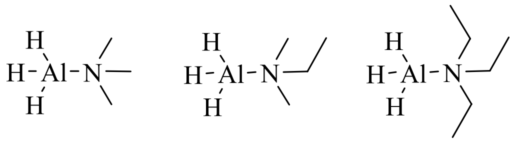
[1] The text was submitted by the authors in English.

Scheme 2. Amine-assisted aluminum hydrides.



Ia **Ib** **Ic**

oxides. The corresponding bisphosphines were obtained with high yields (Table 2, compounds **IIIo–IIIr**).

The above method was efficient with phosphine sulfides leading to high yields of the corresponding products of reduction (Table 3, compounds **IIIa–IIIq**).

EXPERIMENTAL

The reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC) and used with dehydration purification.

The products were elucidated with ^{1}H and ^{31}P NMR spectrometry. NMR spectra were registered on Bruker Advance 400 and 300. TLC of the reaction mixtures and products was performed with commercial 100–400 mesh silica gel plates (GF$_{254}$).

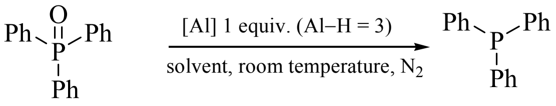
Compound IIIa *(general procedure).* Triphenylphosphine oxide or sulfide (1 mmol), dry hexane (1 mL), and Ic (1 mmol) were added to a Schlenk tube under the atmosphere of nitrogen. The reaction was carried out at room temperature for 10 min and monitored by TLC. Upon completion of the process the reaction mixture was filtered by silica gel and washed several times with ethyl acetate. Ethyl acetate was evaporated and the residue purified by flash chromatography on silica gel with pure cyclohexane to afford the desired phosphine. The yield was determined by GC without additional purification. Names of products, solvents used, and their yields are listed below.

Triphenylphosphine (**IIIa**) [20], hexane, 95%. Diphenylphosphine (**IIIb**) [20], hexane, 93%. Methyldiphenylphosphine (**IIIc**) [20], hexane, 97%. Methoxymethyldiphenylphosphine (**IIId**) [20], hexane, 96%. Ethyldiphenylphosphine (**IIIe**) [28], hexane, 95%. Cyclohexyldiphenylphosphine (**IIIf**) [20], hexane, 92%. Tricyclohexylphosphine (**IIIg**) [20], hexane, 95%. Tributylphosphine (**IIIh**) [20], hexane, 96%. *tert*-Butylmethylphenyl phosphine (**IIIi**) [16], hexane, 97%. Dimethylphenylphosphine (**IIIj**) [16], hexane, 98%. Tris(4-chlorophenyl)phosphine (**IIIk**) [16], hexane, 92%. Tris[4-(trifluoromethyl)phenyl]phosphine (**IIIl**) [16], hexane, 88%. Tri-*p*-tolylphosphine (**IIIm**) [25], hexane, 96%. Tris(4-methoxyphenyl)phosphine (**IIIn**) [25], hexane, 98%. 3,5-Difluorophenylmethylphenylphosphine (**IIIo**) [16], hexane, 94%. 1,2-Bis(diphenylphosphino)ethane (**IIIp**) [16], hexane, 92%. 1,1'-Bis(di-phenylphosphino)ferrocene (**IIIq**) [26], hexane, 93%. 2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene (**IIIr**) [16], hexane, 96%.

CONCLUSIONS

Reduction of tertiary phosphine oxides and sulfides into the corresponding phosphines supported by amine-assisted aluminum hydrides was determined to be efficient. The method is characterized by mild conditions, short reaction time, high efficiency, and significantly expanded substrate scope. This new method is the alternative to current methods of

Table 1. Screening of reduction conditions of TPPO (**IIa**) with amine-assisted aluminum hydrides[a,b]



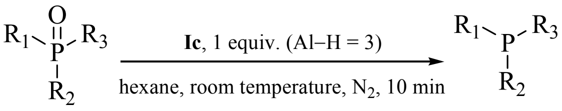
IIa **IIIa**

Entry no.	Comp. no.	Solvent	Yield, %
1	**Ia**	THF	93
2	**Ib**	THF	92
3	**Ic**	THF	95
4	**Ic**	Toluene	91
5	**Ic**	Hexane	97
6	**Ic**	Ethyl ether	93
7	**Ic**	CH_2Cl_2	89
8	**Ic**	MeCN	64
9	**Ic**	DMSO	54
10	**Ic**	DMF	57
11	None	Hexane	Trace

[a] Reagents and conditions: nitrogen atmosphere, triphenylphosphine oxide (1 mmol), Cat [Al] loading (1 mmol), solvent (1 mL), room temperature, 10 min.

[b] Yield (%) as determined by GC.

Table 2. Reduction of phosphine oxides[a,b]



II **III**

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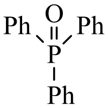
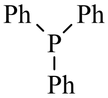
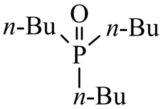
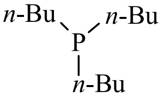
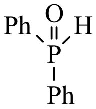
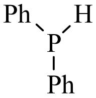
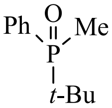
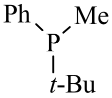
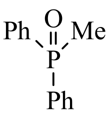
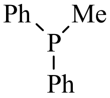
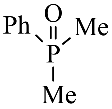
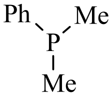
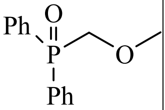
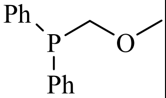
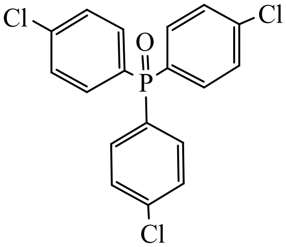
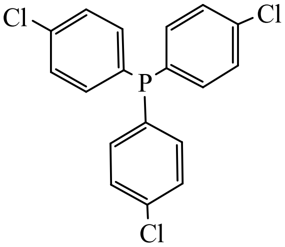
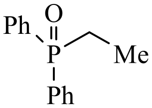
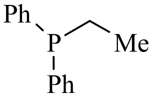
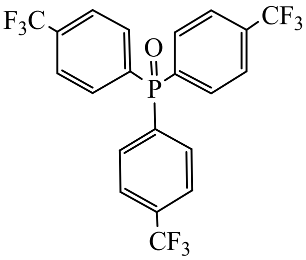
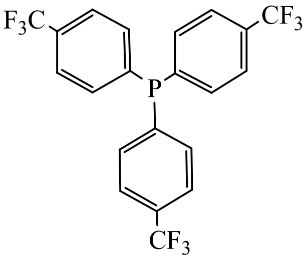
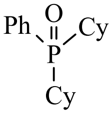
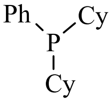
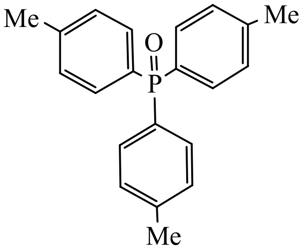
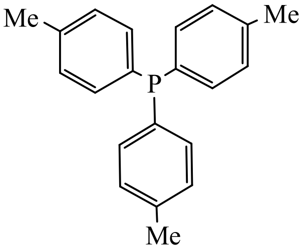
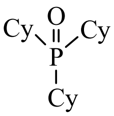
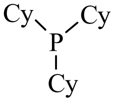
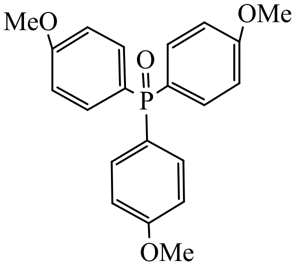
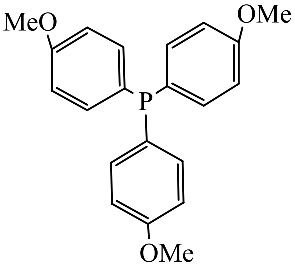
IIIa			95	**IIIh**			96
IIIb			93	**IIIi**			97
IIIc			97	**IIIj**			98
IIId			96	**IIIk**			92
IIIe			95	**IIIl**			88
IIIf			92	**IIIm**			96
IIIg			95	**IIIn**			98

Table 2. (Contd.)

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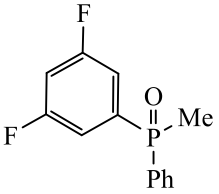
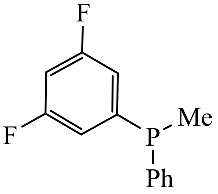
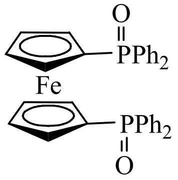
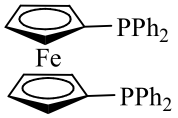
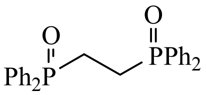
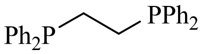
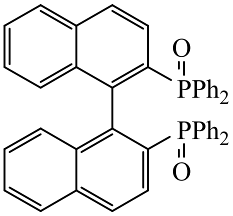
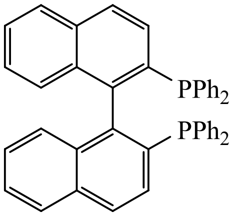
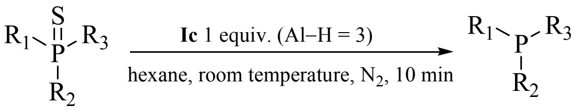
IIIo			94	**IIIq**			93
IIIp[c]			92	**IIIr**			96

[a] Reagents and conditions: nitrogen atmosphere, phosphine oxides (1 mmol), **Ic** (1 mmol), hexane (1 mL), room temperature, 10 min.

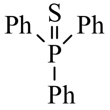
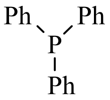
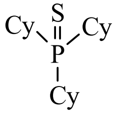
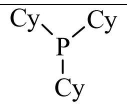
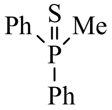
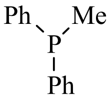
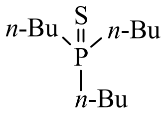
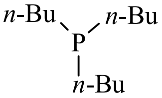
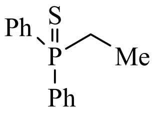
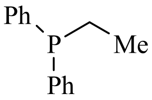
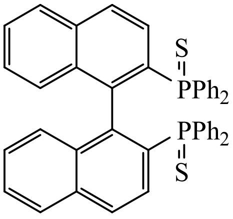
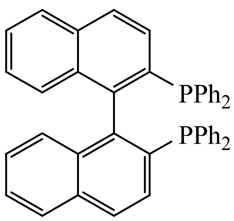
[b] Yield (%) as determined by GC.

[c] **Ic** (2 mmol).

Table 3. Reduction of phosphine sulfides[a,b]



IV **III**

Comp. no.	Substrates	Product	Yield, %	Comp. no.	Substrates	Product	Yield, %
IIIa			92	**IIIf**			91
IIIb			89	**IIIh**			92
IIId			93	**IIIq**[c]			88

[a] Reagents and conditions: nitrogen atmosphere, phosphine sulfides (1 mmol), **Ic** (1 mmol), hexane (1 mL), room temperature, 10 min.

[b] Yield (%) as determined by GC.

[c] **Ic** (2 mmol).

reduction of phosphine oxides and recycling of phosphines engaged in organic reactions.

ACKNOWLEDGMENTS

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