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Arnaud Voituriez, Nidal Saleh

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From Phosphine-Promoted to Phosphine-Catalyzed Reactions by *in situ* Phosphine Oxide Reduction

Arnaud Voituriez* and Nidal Saleh

Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1 av. de la Terrasse, 91198 Gif-sur-Yvette, France.

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ABSTRACT

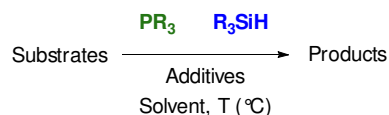
Abstract: The well-known stoichiometric phosphine-promoted reactions such as the Wittig, Mitsunobu, Staudinger, Appel reactions and others are widely used in organic chemistry. Recently, many efforts have been made to render these reactions catalytic in phosphine. Besides decreasing wastes, these catalytic reactions have the advantage to facilitate the purification of the products. The regeneration of the active catalyst was possible by means of reagents that reduces *in situ* the phosphine oxide formed during the reaction. Through this *digest*, we will summarize results on newly developed phosphine-catalyzed reactions.

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Introduction

Phosphines play a key role as stoichiometric reagents in a variety of reactions in which, most of the time, the phosphine is oxidized. Among those, the reactions of Wittig, Staudinger, Appel, Mitsunobu, and others can be cited.^{1,2} While they are very efficient, these transformations generate a significant amount of wastes which complicates their purifications. To aim towards a more environmentally friendly chemistry, a catalytic amount of phosphine should be ideally employed. To reach this goal, a stoichiometric quantity of a reducing agent, such as a silane, is needed to chemoselectively reduce the phosphine oxide formed during the reaction. The reducing agent must be minutely chosen to avoid reducing and/or degrading the various substrates, products or intermediates. The pioneer work of O'Brien, with the development of the first Wittig reaction catalytic in phosphine,³ was the cornerstone for new studies concerning the development of reactions using catalytic quantities of phosphine instead of large quantities. In this *digest*, we propose to reference the methodologies used to develop catalytic versions of numerous well-known reactions, and to highlight in each case the phosphine, the reducing agent, the additives and the reaction conditions used. Indeed, as we will see throughout this review, each reaction should be optimized carefully to obtain satisfying yield and/or selectivity. In the framework of this *digest*, we will not address the catalytic strategies involving activation of the phosphine oxide with isocyanates⁴ or oxalyl chloride,⁵ as these have already been reviewed recently.^{6,7}

To render a reaction catalytic in phosphine, it is fundamental to optimize carefully the reaction conditions. For that purpose, at least four parameters can be assessed: the phosphine, the reducing agent (usually a silane), the addition of some additives to facilitate the *in situ* phosphine oxide reduction, and the solvent (and by extension the concentration and the reaction temperature) (Scheme 1).



Scheme 1. Development of phosphine-catalyzed reactions.

Concerning the use of these reagents and additives, we can set some guidelines that are going to be useful afterward for the development of other phosphine-catalyzed reactions:

(1) The phosphine should be nucleophilic enough to catalyze some reactions. On one hand, acyclic electron-rich phosphines, substituted with alkyl substituents, seem to be at first sight the ideal catalysts. They possess good nucleophilicity, but the corresponding phosphine oxides are also difficult to reduce. On the other hand, cyclic phosphines, such as phenylphospholane oxide, are more easily reducible by silanes than acyclic phosphines, such as triphenylphosphine oxide. Indeed, during the reduction process, the pseudo-tetragonal geometry of the phosphorus atom becomes trigonal bipyramidal.⁸ The energetic barrier related to this geometrical transformation is lowered by

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