



A procedure for Appel halogenations and dehydrations using a polystyrene supported phosphine oxide



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ABSTRACT

The conversion of a commercially available polystyrene supported phosphine oxide into synthetically useful polymeric halophosphonium salts using oxalyl chloride/bromide takes place at room temperature in 5 min and generates only CO and CO₂ as by-products. The polymeric halophosphonium salts so obtained are useful reagents for Appel halogenations and other dehydrative coupling reactions. This gives rise to a simple three-step synthesis cycle for Appel and related reactions using a commercially available polymeric phosphine oxide with very simple purification and no phosphorus waste.

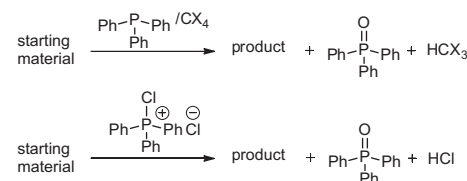
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Phosphorus(V) reagents have been employed extensively in chemical synthesis since the 1960s.¹ For example, one particularly effective reagent system that has found a very widespread application is the phosphine/carbon tetrahalide system, usually referred to as the “Appel conditions”. This reagent combination has been used to effect halogenations of alcohols and carboxylic acids as well as a range of other dehydrative processes with wide substrate scope (Scheme 1A).² An alternative to the carbon tetrahalide system involves the use of chlorotriphenylphosphonium chloride (Scheme 1A) to carry out analogous transformations.³ Although this reagent is commercially available it is prone to hydrolysis and, therefore, is often prepared in situ by the treatment of triphenylphosphine with chlorine, phosgene, or more conveniently, with hexachloroethane or triphosgene.⁴

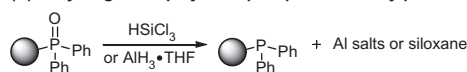
Regardless of which particular protocol is employed, once the desired reaction is complete, the phosphine oxide by-product must be removed to obtain pure material and this purification is often difficult to achieve. Indeed, a wide variety of methods have been developed over the years to alleviate purification difficulties. Some of the most effective methods involve the use of polymeric⁵ or tagged phosphine reagents,⁶ which can either be removed by filtration or undergo phase switching (e.g. to facilitate aqueous extraction) once the reaction is complete.⁷ Since Hodge's report on the use of 1% cross-linked polystyrene-containing phosphine residues for reactions under Appel conditions appeared in 1983,⁸ there has been a great deal of progress in the development of supported or tagged phosphine reagents. Notable work in this area

includes Ley's bipyridyl tagged phosphine reagent⁹ and recent work using monolithic phosphines,¹⁰ Porco's anthracene tagged reagent,¹¹ Curran's fluoros phosphines,¹² Charette's tetraaryl supported phosphines,¹³ Janda's PEG-based polymers,¹⁴ Toy's Rasta Resin,¹⁵ and Barrett's strategy of impurity annihilation involving a tagged diazodicarboxylate and a polymeric phosphine.¹⁶ While these systems greatly simplify purification the subsequent reductive recycling of the phosphorus reagent can be less straightforward because the reduction of triarylphosphine oxides¹⁷ requires relatively harsh reaction conditions using metal hydrides¹⁸ or silane reagents (Scheme 1B).¹⁹ While some recent methods have greatly improved this process, particularly with regard to functional group tolerance,²⁰ the reduction of polymeric phosphine oxides is more difficult still and has received much less attention.²¹

(A) Two protocols for Appel reactions



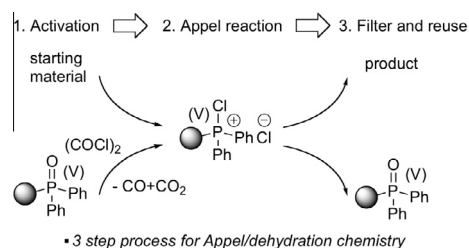
(B) Recycling of the polymeric phosphine oxide by-product



Scheme 1. (A) Appel reactions using a phosphine/CX₄ combination and a chlorophosphonium salt. (B) Reductive recycling of polymeric phosphine oxides.

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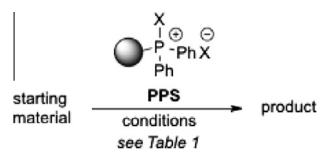
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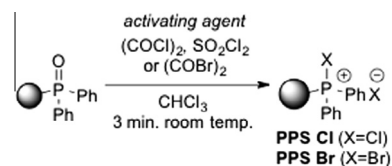
Scheme 2. A three-step process for Appel reactions using a polymeric phosphine oxide.

In this Letter we describe a different approach to the use of polymeric phosphorus(V) reagents, which involves the use of a polystyrene-bound phosphine oxide for Appel and related transformations (Scheme 2). This redox-neutral approach,²² complements existing catalytic phosphorus-mediated reactions,^{23,24} and differs from previous work using supported or polymeric phosphorus reagents because it obviates the need for difficult reductive recycling of the polymeric phosphorus reagent.²⁵ A further significant advantage of the new three-step protocol is that the only by-products associated with the activation step are carbon dioxide and carbon monoxide.

Table 1
Representative reactions with polystyrene-supported halophosphonium salts³⁴



Entry	Starting material	PPS reagent	Conditions	Product	Yield
1		PPS Cl	CHCl ₃ 60 °C 18 h		>95%, run 1 >95%, run 2 >95%, run 3
2		PPS Br	CHCl ₃ 60 °C 18 h		90%
3		PPS Cl	DCE 75 °C 18 h		90%
4		PPS Cl	DCE 75 °C 18 h		84%
5		PPS Cl	CHCl ₃ 60 °C 18 h		>95%, run 1 >95%, run 2 >95%, run 3
6		PPS Cl	DCE 75 °C 18 h		57%
7		PPS Cl	CHCl ₃ 60 °C 18 h		>95%
8		PPS Cl	CHCl ₃ 60 °C 18 h		>95%, run 1 >95%, run 2 >95%, run 3
9		PPS Cl	CHCl ₃ 60 °C 18 h		>95%
10		PPS Cl	CHCl ₃ 60 °C 18 h		86%
11		PPS Cl	CHCl ₃ 60 °C 18 h		85%



Scheme 3. Conversion of polystyrene-supported phosphine oxide into polymeric halophosphonium salts.³³

The present study is based on the transformation of phosphine oxides into chlorophosphonium salts using oxalyl chloride at room temperature, as originally reported in 1977 by Fukui.²⁶ This under-appreciated reaction has been recently exploited by us in catalytic Appel reactions,²⁴ and in other contexts by Tanaka²⁷ and Gilheany to achieve phosphine oxide reductions.²⁸ However, to the best of our knowledge, the conversion of polystyrene-supported phosphine oxides into chlorophosphonium salts using this reagent has not been reported. We began by establishing optimum conditions for the conversion of a commercial polystyrene-supported phosphine oxide²⁹ (Scheme 3). It should be noted that although we opted to use a commercial phosphine oxide the methods of Toy¹⁵ and Charette³⁰ can be used to prepare a variety of polystyrene-supported phosphines from which the corresponding oxides

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