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

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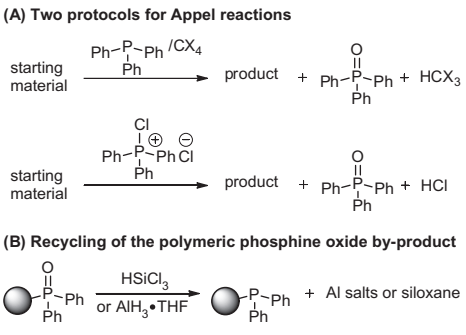
ABSTRACT

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 CO_2 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.

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 polymeric[5] 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 reagent[9] and recent work using monolithic phosphines,[10] Porco's anthracene tagged reagent,[11] Curran's fluorous 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 oxides[17] requires relatively harsh reaction conditions using metal hydrides[18] 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]



Scheme 1. (A) Appel reactions using a phosphine/CX_4 combination and a chlorophosphonium salt. (B) Reductive recycling of polymeric phosphine oxides.

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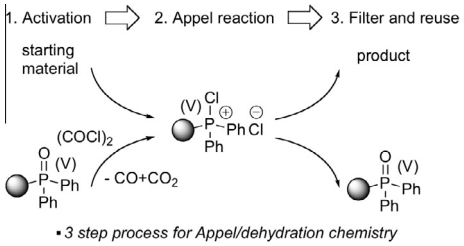
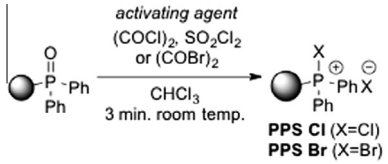


Scheme 2. A three-step process for Appel reactions using a polymeric phosphine oxide.

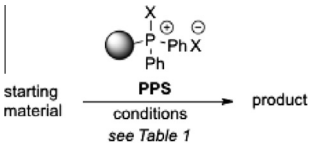
In this Letter we describe a different approach to the use of polymeric phosphorus(V) reagents, which involves the use of a polystyrene-bound phosphine oxide for Appel and related transformations (Scheme 2). This redox-neutral approach,[22] complements existing catalytic phosphorus-mediated reactions,[23,24] 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.

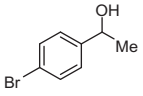
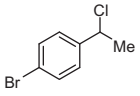
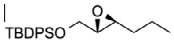
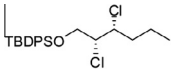
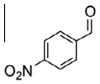
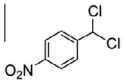
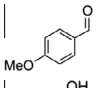
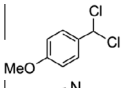


Scheme 3. Conversion of polystyrene-supported phosphine oxide into polymeric halophosphonium salts.[33]

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 underappreciated reaction has been recently exploited by us in catalytic Appel reactions,[24] and in other contexts by Tanaka[27] 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 oxide[29] (Scheme 3). It should be noted that although we opted to use a commercial phosphine oxide the methods of Toy[15] and Charette[30] can be used to prepare a variety of polystyrene-supported phosphines from which the corresponding oxides

Table 1
Representative reactions with polystyrene-supported halophosphonium salts[34]



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%

could be obtained. We were pleased to observe that, upon suspension of the polymeric phosphine oxide in chloroform and treatment with two equivalents of either oxalyl chloride, oxalyl bromide, or sulfuryl chloride (Scheme 3) at room temperature, the corresponding halophosphonium salts were formed.[31] Subsequent analysis of the polymeric phosphine oxide via ATR-IR indicated a phosphoryl stretch at 1197 cm^{-1}, which was absent in the halophosphonium salts.

While the utility of polymeric halophosphonium salts has been established[4] we carried out a number of representative halogenation and dehydration reactions in order to exemplify the simplicity and practicality of the protocol for mmol-scale reactions (Table 1). We first examined chlorination of decanol (entry 1). This was accomplished in excellent yield and the decyl chloride product isolated via filtration and evaporation was judged to be pure by ^1H NMR. The recovered polymer was washed with dichloromethane, reactivated, and used for a second chlorination reaction, which took place with no loss in yield. This process was then repeated for a third time, again with no loss in yield of the alkyl chloride. The analogous bromination reaction (entry 2) was carried out using PPS Br under identical conditions. A second chlorination reaction (entry 3) also proceeded in excellent yield. A deoxydichlorination[32] reaction was next investigated (entry 4) and provided the expected *syn*-1,2-dichloride with retention of the silicon protecting group. The conversion of aldehydes into synthetically useful 1,1-dichlorides was next established (entries 5–7).

In the case of entry 5, the reaction was performed three times with the same batch of polymer with no loss in yield. The conversion of oximes into nitriles also proceeded without incident (entries 8–10). Finally, amide coupling was also shown to be viable in good yield (entry 11). In most instances the polymeric halophosphonium salts were used immediately after the evaporation of the solvent. However, a sample of **PPS Cl** retained its activity for the chlorination of decanol after storage in a glass-stopped flask under nitrogen for 16 h.

In summary we have developed a simple protocol for the generation of polymeric halophosphonium salts from phosphine oxides and demonstrated the applicability of the polymeric reagents so obtained for halogenation and dehydration reactions under Appel conditions. The new three-step protocol is simple, generates only gaseous by-products, and allows expensive,[29] polystyrene-supported phosphine oxides to be very easily reactivated and reused. The convenient nature of the activation step and the recent documentation of Appel halogenation reactions in-flow,[10] opens up the possibility of flow-based reactions with integrated regeneration of polymeric phosphorus reagents. The development of such processes is currently underway.

Acknowledgements

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31. Samples of the polymeric phosphine oxide and halophosphonium salts were prepared by grinding in a mortar with a pestle before being analysed via ATR-IR.
32. *Typical procedure for the synthesis of* ***PPS Cl/Br***: Polystyrene-supported triphenylphosphine oxide (see Ref. [29]) (2.50 g, 3.00 mmol) was suspended in $CHCl_3$ (20 mL) and oxalyl chloride/bromide or sulfuryl chloride (1 equiv) was then added over 1 min. Vigorous evolution of gas was observed for approximately 2 min after the addition was complete. After stirring at room temperature for a further 20 min, the solvent was removed in vacuo to afford the white free-flowing polymeric phosphonium salts which were used immediately without further purification.
33. (a) Isaacs, N. S.; Kirkpatrick, D. *Tetrahedron Lett.* **1972**, *13*, 3869; (b) Sonnet, P. E.; Oliver, J. E. *J. Org. Chem.* **1976**, *41*, 3279; (c) Echigo, Y.; Watanabe, Y.; Mukaiyama, T. *Chem. Lett.* **1977**, *1013*; (d) Oliver, J. E.; Sonnet, P. E. *Org. Synth.* **1978**, *58*, 64; (e) Croft, A. P.; Bartsch, R. A. *J. Org. Chem.* **1983**, *48*, 3353; (f) Iranpoor, N.; Firouzabadi, H.; Azadi, R.; Ebrahimzadeh, F. *Can. J. Chem.* **2006**, *84*, 69; (g) Yoshimitsu, T.; Fukumoto, N.; Tanaka, T. *J. Org. Chem.* **2009**, *74*, 696.
34. *Typical procedure for the deoxychlorination and dehydration reactions*: To a suspension of **PSP Cl** or **PSP Br** (6 equiv) in $CHCl_3$ or DCE (20 mL) was added the appropriate substrate(s) e.g. alcohol/aldehyde/epoxide/oxime/carboxylic acid/amine (1 equiv). The mixture was heated at either 60 °C ($CHCl_3$ reactions) or 75 °C (DCE reactions) for 18 h. The reaction mixture was filtered and the filter cake washed with CH_2Cl_2 (2 × 10 mL). The solvent was removed in vacuo to afford the corresponding products, which were either judged pure by ^1H NMR analysis of the crude reaction product or were purified via normal phase silica gel flash column chromatography eluting with a Et_2O/petroleum ether 40–60 solvent mixture. The recovered polymer could be reused without any further manipulation.