Supported Catalysts

DOI: 10.1002/ange.200503599

Tetraarylphosphonium Salts as Solubility-Control Groups: Phosphonium-Supported Triphenylphosphine and Azodicarboxylate Reagents**

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Tremendous effort has been invested over the last few decades to develop novel supports to facilitate organic synthesis. These supports have been used not only to carry out multistep syntheses,[1] but also to bind catalysts, reagents,

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[**] This work was supported by Valorisation-Recherche Québec (VRQ), Valorisation-Recherche s.e.c. (Univalor), and the Université de Montréal. A.A.B. is grateful to the NSERC (PGF B) and FCAR (B2) for postgraduate fellowships.

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and scavengers to facilitate either the purification process of a product or the recovery of a potentially expensive or toxic catalyst or reagent.[2]

A landmark achievement by Merrifield[3] used functionalized cross-linked, insoluble polymers as a solid support.[4] This solid-phase technology revolutionized peptide and polynucleotide synthesis and was soon used to develop solid-supported reagents and catalysts.[5] As an attempt to restore classical homogeneous organic-chemistry conditions, the replacement of insoluble resins by a soluble polymer support became a popular modification.[6] The non-cross-linked support is typically soluble in some solvents and insoluble in others. Among the soluble polymers, polyethylene glycols (PEGs)[7] and non-cross-linked polystyrene (NCLP)[8] have been by far the most widely used for the recovery and recycling of reagents or catalysts. A recent approach using solid supports derived from ring-opening metathesis polymerization (ROMP) has been reported.[9] Silica-bound scavengers or reagents have also been extensively used recently.[10] The rigid and nonswelling backbone of the silica eliminates the issue of solvent compatibility. Complementary approaches have involved linking a catalyst or reagent on a dendrimeric structure[11] or encapsulating it (homogenous or heterogeneous) in some porous species framework.[12]

Another area of interest is the ionic liquids that consist of pyridinium, imidazolium, ammonium, or phosphonium salts.[13] The structural variations of the salts allow modulation of their melting points. The most popular ionic liquid is $[\mathrm{BMIM}]^+[\mathrm{X}]^-$ (BMIM = 1-*n*-butyl-3-methylimidazolium, X = OTf, BF_4, PF_6, SbF_6; Tf = triflate). As ionic liquids are highly polar and non-coordinating solvents, they readily dissolve transition-metal complexes without changing their properties. An additional versatile alternative is to use the fluorous phase.[14] Reagents and catalysts can be labeled with a certain number of fluorine atoms to increase their solubilities in the fluorous phase. Perfluoro protecting groups have been developed, thus allowing a substrate to be temporarily tagged for its purification on a fluorous reverse-phase column or to be soluble in the fluorous phase. Finally, reagents that carry basic or acidic moieties (free or masked),[15] polyaromatic tags,[16] or stilbene tags (precipiton)[17] have also been used. The main advantage of those approaches is the use of low-molecular-weight molecules, which are easy to purify and characterize.

Our interest in phosphorus chemistry led us to contemplate the possibility of using tetraarylphosphonium and related phosphonium salts as potential solubility-control groups for reagents and catalysts. Obviously, our goal was to develop small stable entities that are soluble in well-defined solvents but that precipitate completely when a minimum amount of an orthogonal solvent is added. The alkyltriarylphosphonium compounds are readily used as ylide precursors for the Wittig reaction. A general characteristic of these reagents is their insolubility in diethyl ether.[18] As diethyl ether is a good solvent for most organic compounds, we first considered quantifying the solubility of some arylphosphonium salts with various counterions (X = Br, ClO_4, PF_6) in a system of CH_2Cl_2/Et_2O. Several arylphosphonium salts were dissolved in CH_2Cl_2, and the amount of Et_2O required to achieve a quantitative precipitation was evaluated by ^{31}P NMR spectroscopic analysis with triphenylphosphine as the internal standard (Figure 1). Two general trends were observed: the amount of diethyl ether required to obtain a quantitative precipitation of the arylphosphonium salts is counterion dependent (Br > ClO_4 > PF_6), and the amount of diethyl ether required is generally less for tetraarylphosphonium salts than for triarylalkylphosphonium salts for the same counterion.

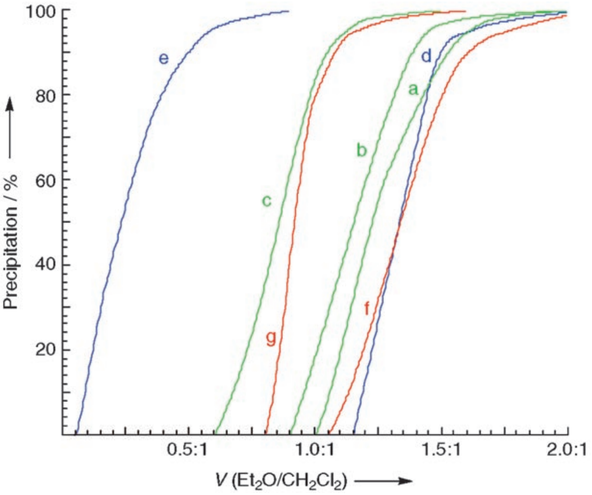


Figure 1. Relative solubility of arylphosphonium salts in Et_2O/CH_2Cl_2. Ph_3PMe; a) Ph_4PX, X = Br; b) Ph_4PX, X = ClO_4; c) Ph_4PX, X = PF_6; d) Ph_4PX, X = Br; e) Ph_4PX, X = ClO_4, X = PF_6 (insoluble); f) **3**; g) **5**.

Another unique property of tetraarylphosphonium salts is that they have little propensity to trap organic compounds upon precipitation under these conditions. This behavior is an important property that supports for reagents and catalysts should ideally possess. For example, when diethyl ether was added to a solution containing Ph_4PBr and sudan red 7B (Figure 2A), quantitative precipitation of an easily filtered

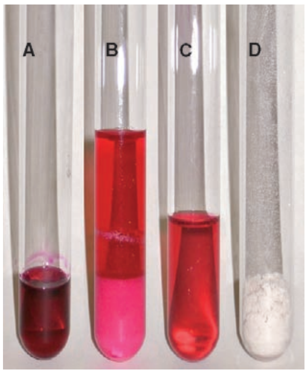
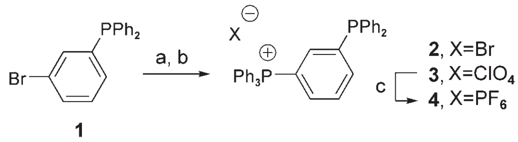


Figure 2. Precipitation/filtration/dissolution sequence of a solution of Ph_4PBr and sudan red 7B. A) Ph_4PBr (250 mg), sudan red 7B (5 mg), and CH_2Cl_2 (1 mL); B) addition of Et_2O (3 mL); C) filtrate; D) filtered phosphonium salt (247 mg) after washing with Et_2O (25 mL) and drying.

solid occurred (Figure 2B). Filtration produced a clear red solution of the dye exempt of phosphonium (Figure 2C) and a clean, white solid (Figure 2D).

In light of these promising properties, we evaluated the ability of this group to control the solubility properties of a supported reagent. To insure improved chemical stability, a tetraarylphosphonium group was selected as the solubility-control group. Furthermore, we assumed that the shielding of the phosphorus center by the four aryl moieties should lead to more reproducible solvent interactions and interionic distances that are largely responsible for the solubility properties.[19] Two recent reviews dealing with the advances in the separation-friendly reagents for the Mitsunobu reaction[20] confirmed the great interest of the chemical community in settling the problems of the elimination of phosphine oxide and hydrazine by-products. We felt that the elaboration of a phosphonium-supported triphenylphosphine moiety would constitute an excellent model to evaluate the efficiency of the tetraarylphosphonium species as a potentially useful solubility-control group. The desired compound **2** was synthesized using the Horner reaction,[21] which involved a nickel-mediated coupling of bromophosphine **1** and triphenylphosphine (Scheme 1). A subsequent anion-exchange reaction led either to the perchlorate or hexafluorophosphate salts **3** and **4**.



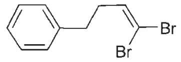
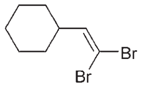
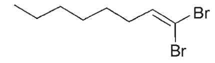
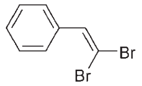
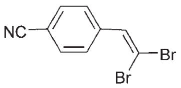
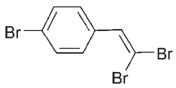
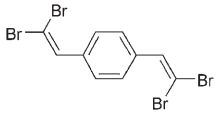
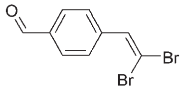
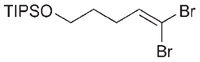
Scheme 1. Reagents and conditions: a) $NiBr_2$, PPh_3, PhCN, reflux, 4 h (78%); b) $LiClO_4$, MeCN, CH_2Cl_2, 15 min (95%); c) $LiPF_6$, MeCN, CH_2Cl_2, H_2O, 1 h (95%).

Gratifyingly, the solubility of both the phosphine **3** and the related phosphine oxide **5** closely followed that of the parent tetraphenylphosphonium salt, thus indicating the predominant influence of the solubility-control group (Figure 1, curves f and g). Both compounds were precipitated quantitatively when a two-volume excess of diethyl ether or less was added.

Although the perchlorate ion is known to be both a powerful oxidant (perchloric acid[22]) and a solid-rocket propellant (ammonium perchlorate[23]), its nonlability in the present compounds makes it slow to react.[24] However, as little chemistry is known regarding tetraarylphosphonium perchlorate, a thermogravimetric experiment was performed to ensure its dynamic thermal stability. The comparison between phosphonium perchlorate and bromide showed comparable behavior: decomposition occurred at a comparable rate and very high temperature (360°C for the perchlorate and 380°C for the bromide).[25] Nevertheless, care must be taken during their use because of the lack of general data about phosphonium percholorate. Alternatively, the hexafluorophosphate salt **4** could be used as well.

With phosphine **3** in hand, its reactivity, recovery, and recyclability were initially tested in the Corey–Fuchs olefination[26,27] as substantial amounts of triphenylphosphine oxide are produced in this reaction. Phosphine **3** was mixed with CBr_4 and zinc dust, and the reaction mixture was heated under reflux prior to the addition of aldehyde. Under these conditions, the ylide was cleanly formed and high yields of the 1,1-dibromoalkenes were obtained (Table 1). The yields obtained with phosphine **3** are usually comparable with those obtained with triphenylphosphine. When the reaction was complete, the zinc salts were filtered and the addition of Et_2O to the filtrate to allow complete precipitation of the phosphine oxide **5** by-product, followed by filtration, led to an organic layer free of phosphine/phosphine oxide. Concentration under reduced pressure afforded a quantitative recovery of a very clean crude product for which the NMR spectroscopic analysis did not show any traces of phosphonium salts (Figure 3).

Table 1: Synthesis of 1,1-dibromoalkenes using the Corey–Fuchs reaction with phosphine **3**.

Entry			Yield [%][a]
1		**6**	94[b]
2		**7**	90[b]
3		**8**	90[b]
4		**9**	96[b]
5		**10**	96[b]
6		**11**	98[c]
7		**12**	95[d]
8		**13**	85[b]
9		**14**	96[b]

[a] After flash chromatography. [b] Phosphine **3** (2.5 equiv), CBr_4 (2.5 equiv), Zn dust (2.5 equiv), CH_2Cl_2 (0.2 M), reflux (0.5 h); then addition of aldehyde, RT, 3 h. [c] Three equivalents of all reagents, RT, 6 h. [d] Six equivalents of all reagents, RT, 6 h.

It is also possible to recycle phosphine **3** in high yield as the only product of the reduction of the resulting phosphine oxide **5** with trichlorosilane and dimethylaniline [Eq. (1)].[28]

Our next study was the Mitsunobu reaction involving relatively hindered secondary alcohols using *p*-nitrobenzoic acid[29] as the nucleophile. Although the optimal solvent for this reaction is THF or toluene, the use of phosphine **3** forced us to opt for a 2:1 mixture of toluene and dichloromethane.

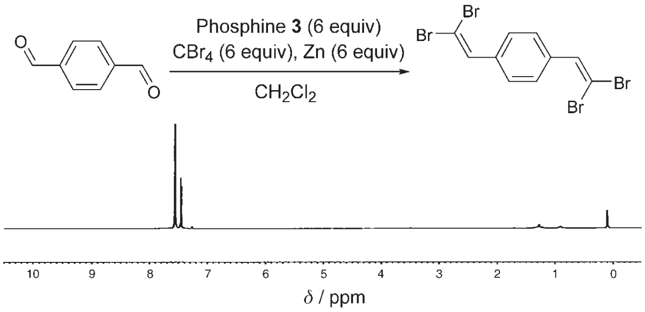
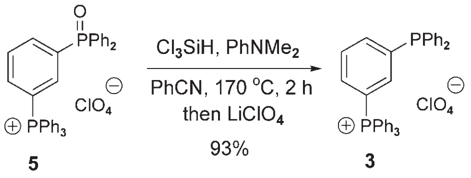


Figure 3. Crude NMR spectrum for the Corey–Fuchs reaction (Table 1, entry 7; quantitative mass recovery).



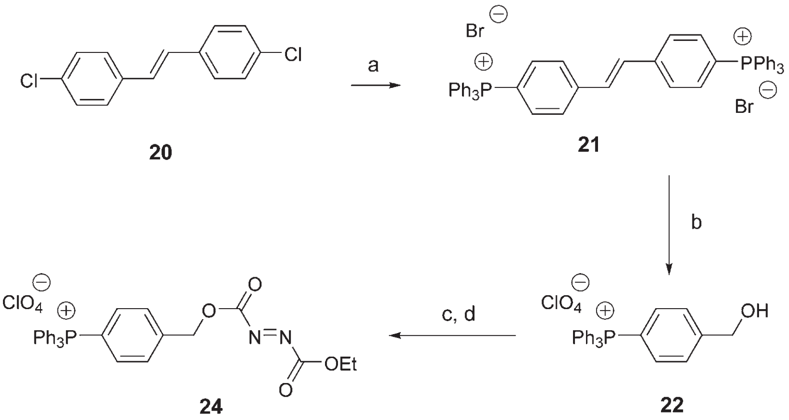
(1)

The results are shown in Table 1, and they indicate that the reactivity of phosphine **3** is quite similar to that of triphenylphosphine.[30] Interestingly, in this solvent system, the phosphine oxide **12** was precipitated, thus allowing a visual indication of the reaction progress. When the reaction was complete, 5 volumes of Et_2O (relative to CH_2Cl_2) were added to complete the precipitation of the phosphonium-derived by-products. Filtration and concentration of the crude mixture led to a phosphorus-free product, as determined by ^{31}P NMR spectroscopic analysis. Conversely, the NMR spectroscopic analysis of the phosphonium salt showed only traces of the reaction products (less than 2%). The Mitsunobu reaction of several alcohols led to esters **15**–**18** in yields comparable to those obtained with triphenylphosphine or other supported phosphines (Table 1, entries 1–4) and with complete inversion of configuration (determined by HPLC for **17**).

The next step was to develop a diethyl azodicarboxylate (DEAD) reagent supported on the phosphonium solubility-control group and examine whether it can be used in conjunction with phosphine **3**. The direct Horner reaction of triphenylphosphine with 4-chlorobenzaldehyde did not give a clean phosphonium salt. Alternatively, a double Horner reaction of 4,4′-dichlorostilbene[31] led to the clean formation of the bis(phosphonium) salt **21**. After an anion-exchange reaction and reductive ozonolysis, benzyl alcohol **22** was obtained in an 77% overall yield from **20**. The elaboration of the DEAD reagent was accomplished by treatment of **22** with triphosgene to generate the chlorocarbonyl pyridinium intermediate followed by the addition of ethyl carbazate to lead to hydrazine dicarboxylate **23**. A final oxidation with *N*-bromosuccinimide (NBS)[32] afforded the DEAD reagent **24** in excellent yield (Scheme 2). The desired product was therefore obtained in five steps and 60% overall yield from 4-chlorobenzaldehyde without the need to purify any of the intermediates by chromatography.

The Mitsunobu reaction of 2-octanol with 4-nitrobenzoic acid, phosphine **3** (1.5 equiv), and DEAD **24** (1.5 equiv) led to the clean formation of the ester (Table 2, entry 3). Addition of diethyl ether followed by filtration allowed quantitative removal of the by-products. To the best of our knowledge, this case is the first time that two supported reagents are used simultaneously with such effectiveness. In a recent report, Hanson and co-workers[33] used five equivalents of both reagents supported on a soluble ROMP polymer to esterify a primary alcohol in 64% yield.

In conclusion, we have developed a highly reactive triphenylphosphine and DEAD reagent supported on a novel solubility-control group. The main advantage of this system is the use of a novel low-molecular-weight support that is soluble in solvents of medium polarities (CH_3CN, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), CH_2Cl_2, $ClCH_2CH_2Cl$, etc.) for the attachment of reagents and insoluble in solvents of low polarities (Et_2O, PhMe, hexane) for clean precipitation. In addition, the reagents display a similar reactivity to their parent nonsupported analogues, there is no need to use extra equivalents because of the availability of all the reactive sites, and the reactions can easily be followed by NMR spectroscopic and mass-spectrometric analysis. Furthermore, they are not hygroscopic (completely insoluble in water) and are easily handled solids that can be quickly and easily be filtered upon precipitation. We are currently introducing additional reagents, catalysts, and substrates on the phosphonium support, and the results will be reported in due course.

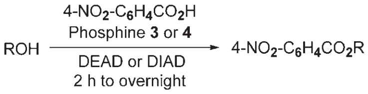


Scheme 2. Synthesis of the DEAD reagent. Reagents and conditions: a) $NiBr_2$, PPh_3, PhCN, reflux, 2 h; b) $LiClO_4$, CH_2Cl_2, MeOH, 15 min, O_3, −78 °C then $NaBH_4$ (77% for two steps); c) triphosgene, pyridine, CH_2Cl_2, −78 °C then $EtOOCNHNH_2$, −78 °C→RT (95%); d) pyridine, NBS, 0 °C, 0.5 h (91%).

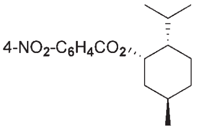
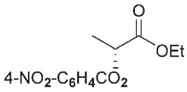
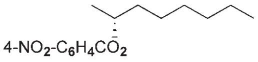
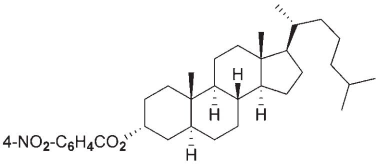
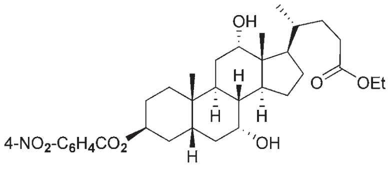
Received: October 11, 2005

Keywords: phosphonium ions · phosphorus · separation · supported catalysts · Wittig reaction

Table 2: Mitsunobu reactions with phosphine **3**.



$$\mathrm{ROH}\xrightarrow[\text{DEAD or DIAD, 2 h to overnight}]{\text{4-NO}_2\text{-C}_6\text{H}_4\text{CO}_2\text{H, Phosphine } \mathbf{3} \text{ or } \mathbf{4}}\text{4-NO}_2\text{-C}_6\text{H}_4\text{CO}_2\text{R}$$

Entry	ROH		Yield [%][a]	Yield [%][f]
1		**15**	79[b] 84[c]	65–84
2		**16**	83[b]	71–91
3		**17**	91[b] 84[d]	83
4		**18**	78[b]	70–89
5		**19**	89[e]	–

[a] After flash chromatography. [b] Phosphine **3** and DEAD reagent. [c] Phosphine **4** and DEAD reagent. [d] Phosphine **3** and azodicarboxylate **24** at −10°C. [e] Phosphine **3** and DIAD reagent. [f] PPh$_3$ or other supported systems.[18,27,29]

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