The preparation and use of polyHIPE-grafted reactants to reduce alkyl halides under free-radical conditions

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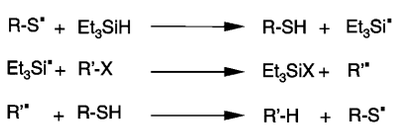
PolyHIPE-supported tin hydride and thiol are synthesized to reduce alkyl bromides under free-radical conditions, taking advantage of the fully interconnected polyHIPE structure. Radical reduction of 1-bromoadamantane, 6-bromohex-1-ene and 1-allyloxy-2-bromobenzene are performed using two methodologies: one using supported tin hydride as reducing agent, and another using supported thiol as polarity-reversal catalyst in the presence of triethylsilane as reducing agent. The polyHIPE-supported tin hydride is used either in catalytic or stoichiometric amounts depending on the bromo compound to be reduced. In the case of unsaturated bromides, both methodologies lead to reductive cyclization, thus enabling radical rearrangement before hydrogen transfer. PolyHIPE-supported organotin hydride is a good alternative to tributyltin hydride to prevent tin contamination and facilitate product separation. PolyHIPE-supported thiol, in the presence of an excess of triethylsilane, shows good activity and selectivity toward reductive cyclization products. Results obtained by the two methodologies are compared and discussed.

Introduction

Free radical reactions such as dehalogenation of alkyl, vinyl or aryl halides, often followed by intra- or inter-molecular C–C coupling are in increasing use in organic synthesis[1] since a large variety of functional groups is tolerated thereby avoiding the necessity of laborious protection and deprotection sequences. These reactions are generally performed at the laboratory stage with tributyltin hydride. However, the toxicity of this reactant is now well established[2] and this drawback strongly limits the development of its use in the synthesis of pharmaceutical derivatives. A less toxic alternative consists in the combination of triethylsilane, the reducing agent, with small amounts of a thiol, as proposed by Roberts and co-workers.[3] Reduction proceeds by a radical-chain mechanism and the thiol acts as a polarity-reversal catalyst which mediates hydrogen-atom transfer from the Si–H group of the silane to the alkyl radical (Scheme 1). However this methodology is limited by the stench of thiols.



Scheme 1 Radical-chain mechanism involving the reducing agent Et_3SiH and a polarity-reversal catalyst thiol.

The development of polymer-supported chemistry is one of the main features of modern organic synthesis. The supports generally used in these applications are based on lightly cross-linked styrene/1,4-divinylbenzene (DVB) beads called gel resins. These resins have no permanent porosity, and therefore are usable only in solvents allowing the polyHIPE to swell such as toluene or THF.[4] An impressive amount of work using these resins as supported catalysts,[5] supported reagents[6] and for solid-phase organic synthesis[7] has been reported. The use of macroporous beads with a permanent porosity can be an alternative but is not completely satisfactory because of the poor permeability of these materials[8] and this reduces their usefulness for organic synthesis. An alternative approach consists in the use of porous polymer foams having a low resistance to flow which makes them usable in low-pressure, continuous-flow methods. These materials are well known and have been produced by a wide variety of techniques ranging from leaching soluble fillers through gas-blowing to phase separation, although the structure of these materials is often irregular and difficult to control.[9] A novel method for producing porous materials with a more regular structure has been developed based on high-internal-phase emulsion (HIPE). These foams are called emulsion-derived foams and were initially developed by Unilever[10] and called polyHIPE®. The characteristics and syntheses of such polyHIPE materials have already been reviewed.[11]

Total replacements of soluble organotin hydride by the corresponding polymer-supported reactant are credible alternatives.[12] Indeed, this tin functionalized polymer would prevent tin contamination of the products in solution, tin functionalities remaining attached to the polymer backbone after reaction. Similarly, a thiol function grafted onto a polymer will not be volatile and could be easily separated from the reaction products, avoiding any odorous pollution. The reduction of 'simple' alkyl bromides producing radicals giving no rearrangement would occur similarly, whatever the hydrogen-transfer agent YH involved in solution or grafted on a polymer and present in small or stoichiometric amounts. This could be different when the radical, generated by abstraction of the bromine atom, can rearrange. Thus, the relative amounts of the products UH and RH, obtained under various conditions, may differ because of the existing competition between hydrogen transfer and rearrangement (Scheme 2).

In this paper, we present two types of functionalized

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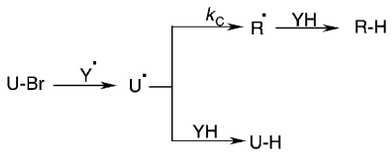
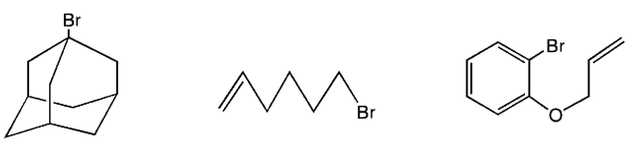


Scheme 2 Competition between hydrogen transfer and rearrangement in radical mechanism.

polyHIPE for free-radical chain reduction. The post-functionalization of a polyHIPE-supported unsaturation led to thiol functionalities after free-radical addition of thioacetic acid and deprotection. Another approach consists in copolymerization of an organotin monomer, styrene and DVB. Using small blocks of both resins, radical reductions of 1-bromoadamantane **1**, 6-bromohex-1-ene **2** and 1-allyloxy-2-bromobenzene **3** (Chart 1) have been investigated. PolyHIPE-supported organotin hydride, denoted ***PH*-SnH**, was used in catalytic amount, with *in situ* regeneration by $NaBH_4$ for **1** and **3** and, in the case of **2**, in stoichiometric amounts because of the possible direct reduction of **2** by $NaBH_4$. PolyHIPE-supported thiol, noted ***PH*-SH**, was used in catalytic amount for the reduction of the three bromo compounds, triethylsilane being the reducing agent.



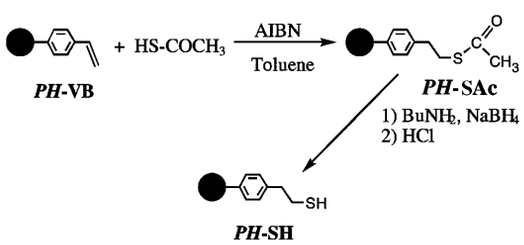
1 2 3

Chart 1 Alkyl bromides used in radical reduction.

Results and discussion

1 Synthesis and physical properties of functional polyHIPEs

The (vinyl)polystyrene polyHIPE was synthesized from a commercial-grade solution of DVB [80% DVB, 20% ethylvinylbenzene (EVB)]. This polyHIPE possesses vinylbenzene groups, hence the term ***PH*-VB**, due to partial polymerization of DVB.[13] This precursor allows a very general and direct route to a wide variety of stable and effective spacer-containing polymers, with mild conditions and good yield. Upon radical or other anti-Markovnikov addition of a reagent H–X, each vinyl becomes a dimethylene spacer supporting a functional group.[14] This dimethylene spacer between the polystyrene aryl and functional group heteroatom has been found to improve stability and activity of polymer-bound reagents and catalysts, compared with the (mono)methylene spacer which makes the carbon–heteroatom bonds relatively fragile.[15] In particular, the addition of thioacetic acid to the pendant vinyl groups, followed by aminolysis, leads to supported mercapto SH functionalities (Scheme 3).



Scheme 3 Preparation of ***PH*-SH**.

In order to synthesize ***PH*-SnH** in the same convenient way, a first trial of the addition of Bu_2SnHCl to the pendant vinyl groups of the precursor ***PH*-VB** was performed. Unfortunately, the resulting polymer was not found to possess, after reduction, a significant amount of Sn–H functionality, since no peak at 1800 cm^{-1} (Sn–H peak assignment) appeared in FT-IR spectroscopic analysis.

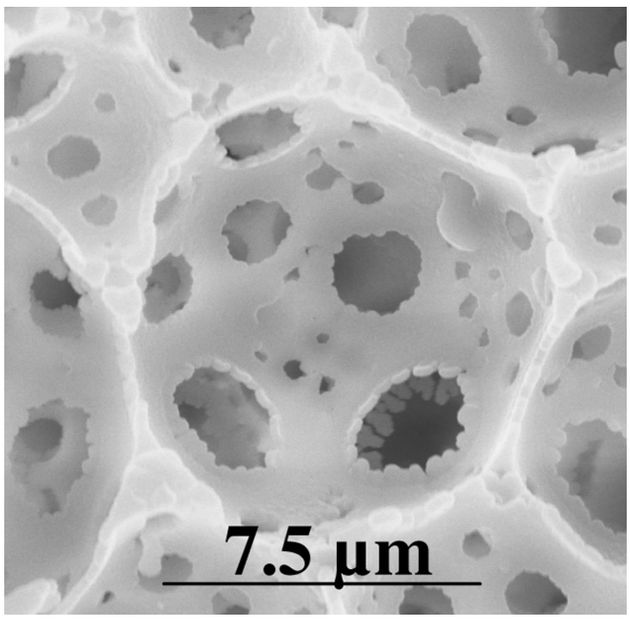
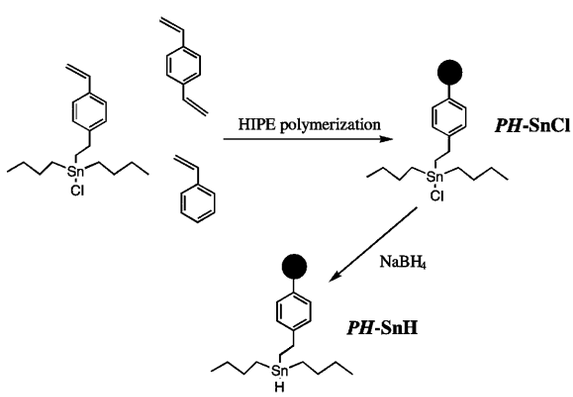


Fig. 1 Scanning electron microscopy of polyHIPE.

An alternative was to prepare a polyHIPE-supported organotin chloride (***PH*-SnCl**) by polymerization of a highly concentrated reverse emulsion obtained from a mixture of 4-[2-(dibutylchlorostannyl)ethyl]styrene[12] as the functional monomer, styrene and DVB as crosslinker. The organotin hydride counterpart (***PH*-SnH**) was produced by reduction of ***PH*-SnCl** with $NaBH_4$ (Scheme 4).



Scheme 4 Preparation of polyHIPE-supported organotin hydride.

A scanning electron micrograph of polyHIPE-supported organotin chloride ***PH*-SnCl** is shown in Fig. 1.

Note the 5–25 µm cells formed by the temporary pore former (water) and the great number of 1–2 µm 'window' between adjacent cells. The characteristic dimension of the cell diameter (about 10 µm) is to be compared with the characteristic window diameter (about 1 µm).

The general range of measurements/properties of the emulsion-derived foam prepared may be summarized as follows:

– macroscopic density as low as 0.05 g cm^{-3}
– internal void volume ≈95%, *i.e.* 95% pore volume/5% polymer
– fully interconnected uniform structure, with cells being connected to all their neighbours, allowing liquids to circulate through the porous structure
– the large channels and the full interconnection allow a worthwhile flow rate under low pressure.

2 Loading of the useful polyHIPE-supported functionalities

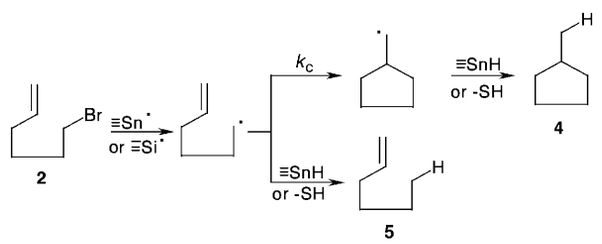
Table 1 reports the functionalization level of ***PH*-SnCl**, ***PH*-SnH** and ***PH*-SH**. We note that about 33% of the Sn–Cl bonds present on ***PH*-SnCl** were transformed into Sn–H bonds by $NaBH_4$. The remaining chlorine atoms were probably too buried inside the material to be easily accessible to the reducing agent.

3 Radical reduction of bromides 1, 2 and 3

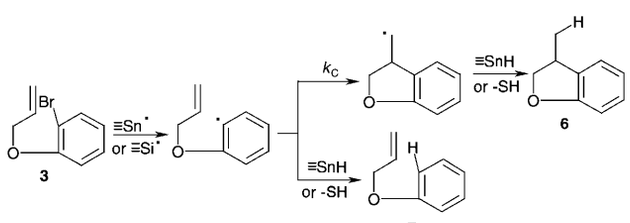
The reduction of 1-bromoadamantane **1** by ***PH*-SnH** and ***PH*-SH**, respectively regenerated *in situ* by reduction of the intermediates by sodium borohydride and triethylsilane, was performed under conditions similar to the reduction of alkyl bromides by supported organotin hydride[12] and dodecanethiol.[3] Table 2 summarizes the relative and overall yields of formed products resulting from the reduction of **1**, using various reducing agents and supported catalysts. The results described in entries 1,3 and 4,6 (Table 2) show that the reduction of **1** is due to the functions grafted onto the polyHIPE *via* the expected free-radical process. The observation of a relatively high conversion in 1 h confirms the efficient regeneration of the hydrogen-transfer agent, thiol or tin hydride, in the reaction of the intermediate, thiyl radical or tin bromide, with the reducing agent respectively employed, triethylsilane and sodium borohydride. The first-hour conversions obtained using polyHIPE-supported chemistry when compared with solution chemistry are lower (entries 2,3 and 5,6). This could be due to slower elementary reactions rates when one of the reactive species is attached to the polyHIPE; this is certainly caused by the diffusion of only the small molecules and radicals towards the backbone of the supported reagents.

Once the efficiency of the supported hydrogen transfer was confirmed, it appeared of interest to study the reduction of unsaturated bromide since the reductive cyclizations of unsaturated halides are useful tools in organic synthesis.[1] Then, the reductions of 6-bromohex-1-ene **2** and of 1-allyloxy-2-bromobenzene **3** were investigated using the polyHIPE reducing agents. These free-radical reactions would produce two major compounds: the products of reductive cyclisation (**4** from **2**, **6** from **3**) and those arising from the direct reduction (respectively **5** and **7**) (Schemes 5 and 6). The results obtained for both substrates are reported in Table 3.

The homolytic reduction of **2** by ***PH*-SnH** (sodium borohydride reduces **2** directly to generate **5**) and **3** by ***PH*-SnCl/** $NaBH_4$ allowed us to perform the reductive cyclization of both bromides with good selectivity (entries 6 and 8). The treatment of **2** and **3** by triethylsilane in the presence of ***PH*-SH**, under the same conditions as the reduction of **1**, did not lead to any of the expected hydrocarbon **4** or **5** from **2** (100% of **2** recovered unchanged); meanwhile the cyclic ether **6** was formed in a yield of 10% from **3** (90% unchanged) after 6 h (Table 3). As pointed out by Roberts,[3] the possible addition of the thiyl



Scheme 5 Radical-reduction mechanism of 6-bromohex-1-ene **2**.



Scheme 6 Radical-reduction mechanism of 1-allyloxy-2-bromobenzene **3**.

Table 1 Loading of the desired polyHIPE-supported functionalities

PolyHIPE	φ[a] (%)	Styrene (mol %)	DVB[b] (mol %)	Tin monomer (mol %)	Loading of functionality (mmol g^{-1})
***PH*-Ac**	95	0	100	0	1.50 (SAc[c])
***PH*-SH**	95	0	100	0	0.30 (SH[d])
***PH*-SnCl**	90	70	20	10	0.34 (SnCl[e])
***PH*-SnH**	90	70	20	10	0.10 (SnH[f])

[a] Volumic fraction of pore former (aqueous phase). [b] 80% commercial solution of DVB. [c] Estimated by S elemental analysis. [d] Estimated by Cl elemental analysis after reaction with trichloroacetyl chloride. [e] Estimated by Sn elemental analysis. [f] Estimated by the amount of decane formed after stoichiometric reaction with 1-iododecane and AIBN.[12]

Table 2 Conversion and reaction conditions of radical reduction of **1** (1-bromoadamantane)

Entry	R-Br	*T*/°C	Catalyst	Reducing agent (equiv.)	Cat./RBr	Reaction time/(*t*/h)	Adamantane yield (%)
1	**1**	80	none	$NaBH_4$ (2)	0	1	5
2	**1**	80	Bu_3SnCl	$NaBH_4$ (2)	0.1	1	100
3	**1**	80	***PH*-SnCl**	$NaBH_4$ (2)	0.1	1	77
4	**1**	80	none	Et_3SiH (2)	0	1	0
5	**1**	80	$C_{12}H_{25}SH$	Et_3SiH (2)	0.02	1	100
6	**1**	80	***PH*-SH**	Et_3SiH (2)	0.02	1	70

Table 3 Conversion and reaction conditions of radical reduction of **2** and **3** by polyHIPEs grafted reagents

Entry	R-Br	*T*/°C	Catalyst	Reducing agent (equiv.)	Cat./RBr	Reaction time/(*t*/h)	Conversion (%)
6	**2**	70	***PH*-SnH**	none	1	10	90 **4** and **5** (84/16)
7	**2**	70	***PH*-SH**	Et_3SiH (2)	0.05	6	0
8	**3**	70	***PH*-SnCl**	$NaBH_4$ (2)	0.1	10	50 **6** and **7** (90/10)
9	**3**	70	***PH*-SH**	Et_3SiH (2)	0.05	6	10

Table 4 Conversion and reaction conditions of radical reduction of **2** by ***PH*-SH**/Et_3SiH (**2**/***PH*-SH** = 0.05; T = 70 °C; 6 h)

Et_3SiH/**2**	2	10	20	40	100
4 Yield (%)[a]	0	5	55	90	100
6 Yield (%)[a]	0	0	0	0	0
Unchanged **2** (%)[a]	100	95	45	10	0

[a] Determined by GLC.

radical to the double bonds present in the medium could be responsible for such an inefficient reduction. The increase in the concentration of the silane would allow direct reaction of the thiyl radical towards the regeneration of the thiol by hydrogen abstraction from the silane and, then, allow the free-radical chain reduction of the unsaturated bromide to occur. The results summarized in Table 4 indicate that the reductive cyclization of **2** could be performed to completion in 6 h with a one hundred fold excess of silane relative to the bromide with ***PH*-SH**.

Comparison of the reductive cyclisation of **2** using ***PH*-SH**/Et_3SiH rather than ***PH*-SnH** shows a higher selectivity with the first reagent, generating only the cyclic product **4**. The possible use of a catalytic system – even with primary alkyl bromide – involving an organic reducer totally soluble in the organic medium (triethylsilane) and this selectivity are good arguments to select the thiol/triethylsilane system instead of the tin one. Nevertheless, it is important to underline the necessary use of a high ratio of silane to thiol to perform the reduction of bromide compounds possessing a terminal vinyl group. This could be a drawback when the required reaction product has a boiling point close to that of triethylsilane (107–108 °C). In this case, the commercial availability of numerous other silanes would allow one to circumvent this problem.

The reductive cyclisation of **3** with the thiol–silane system (***PH*-SH**/Et_3SiH/**3** = 0.05 : 75 : 1) is quantitative in 6 h at 70 °C, while the use of tin catalyst (***PH*-SnCl**/$NaBH_4$/**3** = 0.1 : 2 : 1) produced a mixture of **6** and **7** (respectively 9 : 1) with a yield of only 50%. These results confirmed the superiority of the supported thiol reagent over the tin one.

Experimental

1. Materials

Unless otherwise noted, all materials were purchased from Aldrich Chemical Company and used as received. 4-[2-(Chlorodibutylstannyl)ethyl]styrene, was prepared by hydrostannation of *p*-divinylbenzene with Bu_2SnHCl according to a published procedure.[12] Dibutylchlorostannane was prepared by the reduction of Bu_2SnCl_2.[16]

2. Characterization

Gas chromatographic studies were performed with a VARIAN 3400 coupled to a SPECTRAPHYSIC CHROMJET integrator. The capillary column used was DB5 type (5% Ph), 30 m in length, 0.25 mm in inner diameter and with a film thickness of the stationary phase of 0.25 μm; the carrier gas was nitrogen (0.5 bar).

Scanning electron microscopy was performed with a JEOL 840 ME apparatus. Microanalyses of samples of functional polymers were performed in the 'Service central d'analyse élémentaire' C.N.R.S. (Vernaison, France).
FT-IR spectra were taken with a Perkin–Elmer Paragon 1000 spectrometer.

3. Preparation of *PH*-VB and *PH*-SnCl

In a typical experiment, a volume V_{org} of organic phase generally constituted of styrene, a commercial-grade solution of DVB (80 : 20 DVB : EVB) as cross-linker, eventually a functional co-monomer {4-[2-(chlorodibutylstannyl)ethyl]styrene} and sorbitan monooleate (Span®80) as emulsifying agent (20% w/w of the organic phase) was placed in a reactor. The mixture was stirred with a rod fitted with a D-shaped paddle, connected to an overhead stirrer motor, at approximately 300 rpm. A volume V_{aq} of aqueous phase was prepared separately by dissolving the initiator, potassium persulfate $K_2S_2O_8$, and sodium chloride NaCl (1.5% w/w of the aqueous phase) in distilled water. This solution was added dropwise, under constant mechanical stirring, to the organic solution in order to obtain a thick white homogeneous emulsion without apparent free water. Once all the aqueous phase had been added, stirring was continued for a further 15 min to produce an emulsion as uniform as possible. The high-internal-phase emulsion obtained was then placed in a polyethylene bottle. The polymerization occurred by immersing the plastic bottle in a water-bath, heated to 60 °C for 10 h. The container was then cut away to collect the resulting polymeric monolith. This was extracted with acetone in a Soxhlet apparatus for 48 h, then was dried under vacuum at 60 °C for 48 h. The resulting monolith was cut into cubes (approx. 5 mm per side). The polyHIPE thus synthesized is characterized by the volumic fraction of pore precursor (water) $\varphi = V_{aq}/(V_{aq} + V_{org})$.

4. Preparation of *PH*-SnH

1 mole equivalent (hereafter abbreviated to equiv.) of SnCl from ***PH*-SnCl** (100 mg, 0.034 mmol SnCl) was treated with 20 equiv. of $NaBH_4$ (31 mg, 0.68 mmol) in diethylene glycol bis(methyl ether) (20 mL) at 70 °C for 2 h. The mixture was then filtered and the resulting polymer washed successively with water, ethanol and diethyl ether.

5. Preparation of *PH*-SH

Small cubes of ***PH*-VB** [500 mg, 3.00 mmol C=C g^{-1}, 1.50 mmol C=C] were impregnated with toluene by the freeze/thaw method and suspended in 40 mL of toluene. 5 Equiv. of thioacetic acid (570 mg, 7.50 mmol) and AIBN (1% mol/C=C) were then added. The suspension was heated at 70 °C for 48 h. The polymer was filtered off, extracted with acetone overnight on a Soxhlet apparatus, and dried under vacuum at 60 °C, overnight. FT-IR (KBr) ν_{max} 1690 cm^{-1} (C=O). Elemental analysis: S, 1.50 mmol g^{-1}.

The resulting ***PH*-5Ac** (500 mg, 0.75 mmol SAc) was then treated with 10 equiv. of *n*-butylamine (550 mg, 7.5 mmol) and $NaBH_4$ (4 mg) in DMF (20 mL) to produce ***PH*-SH**.[17]

6. Radical reduction of 1

1 Equiv. of 1-bromoadamantane **1** (73 mg, 0.34 mmol) was reduced by 0.1 equiv. of SnCl (from ***PH*-SnCl** or Bu_3SnCl) (0.034 mmol SnCl) in the presence of 2 equiv. of $NaBH_4$ (26 mg, 0.68 mmol) and AIBN. The mixture was allowed to react at 80 °C in ethylene glycol bis(methyl ether) (10 mL).

1 Equiv. of 1-bromoadamantane **1** (322 mg, 1.50 mmol) was also reduced by 0.02 equiv. of thiol (***PH*-SH** or dodecanethiol) (100 mg, 0.03 mmol) in the presence of 2 equiv. of Et_3SiH (348 mg, 3.0 mmol) and dilauroyl peroxide (0.05 equiv.). The mixture was allowed to react at 80 °C in cyclohexane (10 mL).

7. Radical reduction of 2

1 Equiv. of 6-bromohex-1-ene **2** (8 mg, 0.05 mmol) was reduced by 1 equiv. of SnH from ***PH*-SnH** (500 mg, 0.05 mmol SnH) in the presence of AIBN (0.05 equiv.). The mixture was allowed to react at 70 °C in benzene (10 mL).

In a typical experiment, 1 equiv. of 6-bromohex-1-ene **2** (98 mg, 0.60 mmol) was also reduced by 0.05 equiv. of thiol from ***PH*-SH** (100 mg, 0.03 mmol SH) in the presence of 2 equiv. of Et_3SiH (139 mg, 1.2 mmol) and dilauroyl peroxide (0.05

equiv.). The mixture was allowed to react at 70 °C in *n*-heptane (10 mL).

8. Radical reduction of 3

1 Equiv. of 1-allyloxy-2-bromobenzene **3** (72.5 mg, 0.34 mmol) was reduced by 0.1 equiv. of SnCl from ***PH*-SnCl** (100 mg, 0.034 mmol SnCl) in the presence of 2 equiv. of $NaBH_4$ (26 mg, 0.68 mmol) and AIBN (0.05 equiv.). The mixture was allowed to react at 70 °C in ethylene glycol bis(methyl ether) (10 mL).

1 Equiv. of 1-allyloxy-2-bromobenzene **3** (128 mg, 0.60 mmol) was also reduced by 0.05 equiv. of thiol from ***PH*-SH** (100 mg, 0.03 mmol SH) in the presence of 2 equiv. of Et_3SiH (139 mg, 1.20 mmol) and dilauroyl peroxide (0.05 equiv.). The mixture was allowed to react at 70 °C in *n*-heptane (10 mL).

Conclusions

This work confirms that polyHIPE-supported hydrogen transfer reagents can be:

– obtained by copolymerization of functional monomers or by post-functionalization of a polyHIPE generated from divinylbenzene
– used either in catalytic or stoichiometric amounts to reduce alkyl and aryl bromides under free-radical conditions. This reaction could be synthetically useful according to the possibility of realizing a free-radical rearrangement of the generated alkyl radical, involved in the reduction, before its trapping by the hydrogen-transfer reagent.

The supports used are of great interest since they offer a permanent porosity, providing better accessibility to active sites and allowing a wider range of solvents than do beads prepared by suspension polymerization. The highly interconnected porous structure allows the development of low-pressure continuous-flow application. We are currently developing this strategy in order to improve conversions and optimize polyHIPE-supported functionality efficiency. Indeed, the next step is to use these materials in columns in order to be able to operate chemical transformations in continuous-flow regimes.

PolyHIPE-supported organotin hydride is a good alternative to tributyltin hydride to prevent tin contamination and to facilitate product separation. PolyHIPE-supported thiol used in conjunction with triethylsilane showed good activity, with elimination of odorous pollution, due to the thiol, in the reduction system of Roberts and co-workers.[3] The general possibility of using a catalytic system with a reducer (silane), and its reaction product (halogenosilane) highly soluble in organic solvents, and the use of reactants with no toxicity in this last methodology make it more attractive than the one involving even a grafted tin reagent. However, in the case of the reduction of unsaturated organic halides there is a limitation due to the necessity to operate with a great excess of silane, and then efforts have to be made to define a more reactive silane to trap readily the thiyl radicals before they themselves react with the unsaturated substrates.

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