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Communications

A Polymer-Supported Organotin Hydride and Its Multipurpose Application in Radical Organic Synthesis

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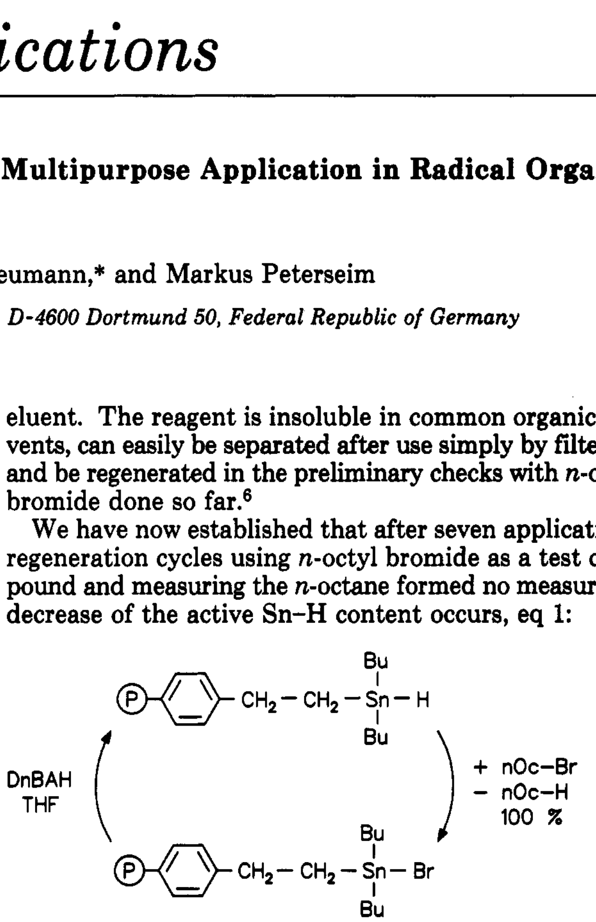
Summary: The multipurpose application of a polystyrene-supported, regenerable organotin hydride for radical organic syntheses is demonstrated using 10 examples taken from dehalogenation of bulky or multifunctional halides, dehydroxylation of secondary alcohols, and deamination of secondary or tertiary amines.

"The dramatic advances in the application of free radical reactions to problems in organic synthesis can be attributed in good measure to the versatility of trialkyltin hydride reagents."[1] The most used tin hydride is tributyltin hydride so far.[2,3] But, "the drawback consists in the separation of .... their consecutive products from the desired reaction products, which is mostly a difficult, and rarely a quantitative one".[4]

Therefore, using earlier experience of this laboratory in hydrostannation,[5] we developed an organotin reagent based on cross-linked polystyrene of large pore size,[6,7] where the tin moiety is separated from the aromatic nucleus by two methylene units and therefore in the chemically utmost stable position. We found no leaching of tin into the eluent. The reagent is insoluble in common organic solvents, can easily be separated after use simply by filtering and be regenerated in the preliminary checks with *n*-octyl bromide done so far.[6]

We have now established that after seven application–regeneration cycles using *n*-octyl bromide as a test compound and measuring the *n*-octane formed no measurable decrease of the active Sn–H content occurs, eq 1:



(1)

We report here the first practical applications of our polymer-supported organotin hydride to three of the most important, most frequently used free-radical reactions:[2,3,8] dehalogenations—which are important, for example, also after atom-transfer mechanisms[1,8]—of bromides or chlorides, dehydroxylation of a secondary alcohol, and deaminations. For a strict comparison of the reactivity and selectivity of the new reagent, we selected examples performed with tributyltin hydride so far.

In order to check for any loss of products by adsorption or workup procedures we used 1–5 mmol experiments and found complete conversions of the reactants into the products indicated exclusively ones (^1H NMR). No side reactions occurred. The yields indicated in eqs 2–8 refer

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[1] Curran, D. P. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluver Academ.; London, 1989, p 37. For a recent review see: Curran, D. P. *Synlett* **1991**, 63.

[2] Neumann, W. P. *Synthesis* **1987**, 665.

[3] Metzger, J. O. In *Houben-Weyl, Meth. d. Organ. Chemie*; Regitz, M.; Giese, B., Eds.; Thieme: Stuttgart, 1989, Vol. E19a, p 153.

[4] Scheffold, R. *Nachr. Chem. Tech. Lab.* **1988**, *36*, 261.

[5] Neumann, W. P.; Pedain, J. *Tetrahedron Lett.* **1964**, 2461.

[6] Gerigk, U.; Gerlach, M.; Neumann, W. P.; Vieler, R.; Weintritt, V. *Synthesis* **1990**, 448. The reactive polymer used in the following is based on a macroporous, 6% cross-linked styrene–divinylbenzene copolymer with an average pore diameter of ca. 620 Å. It will be available from Merck-Schuchardt a. Co., Eduard Buchner Str. 14-20, D-8011 Hohenbrunn, FRG.

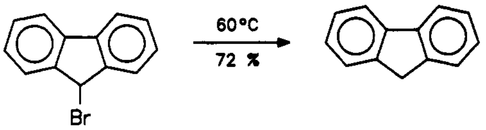
[7] A few earlier approaches to a polymer-supported tin hydride have been reported (1975–1987) and are discussed in detail in ref 6.

[8] Curran, D. P. *Synthesis* **1989**, *417*, 489.

0022-3263/91/1956-5971$02.50/0

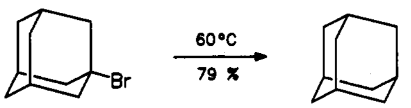
to isolated, pure compounds with correct mp. The workup simply has been done by evaporating the solvent from the reaction mixture after filtering and washing the reactive polymer.[9]

In a first group, we have choosen bulky halides in order to find out whether any problems are caused by insufficient pore size of the polymer, partial inaccessibility of the reactive Sn–H groups, or diffusion through the pores. We could not find any problems. 9-Bromofluorene forms fluorene, eq 2. Both triphenylmethyl bromide and the more stable chloride give triphenylmethane, eq 3. The bridgehead bromide 1-bromoadamantane yields pure adamantane, eq 4.



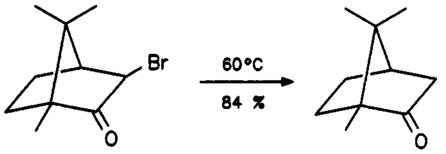
(2)

$$\mathrm{Ph_3C{-}Br} \xrightarrow[82\ \%]{60\ ^\circ\mathrm{C}} \mathrm{Ph_3C{-}H} \xleftarrow[\text{quant.}]{60\ ^\circ\mathrm{C}} \mathrm{Ph_3C{-}Cl} \qquad (3)$$

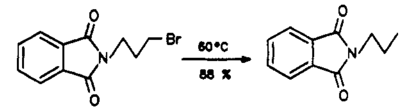


(4)

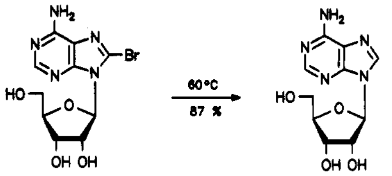
In a second group, we looked for the chemoselectivity of the desired dehalogenations, i.e., for interferences possibly given by other functional groups. 3-Bromocamphor gives camphor exclusively, eq 5, *N*-(3-bromopropyl)phthalimide leads to the alkylated phthalimide, eq 6, without other reactions to be thought of in the presence of Sn–H groups,[10] and 8-bromoadenosine is transformed only to adenosine (in a dry medium), eq 7. Neither the free amino nor the different oxygen functions interfere, as is theoretically possible.[10]



(5)

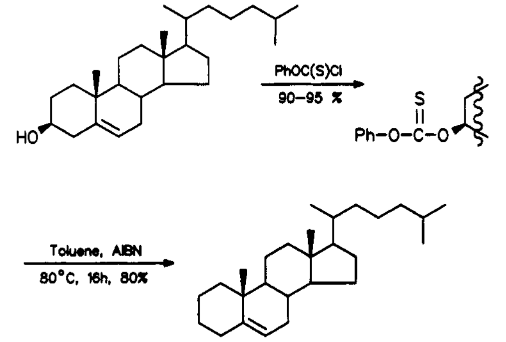


(6)



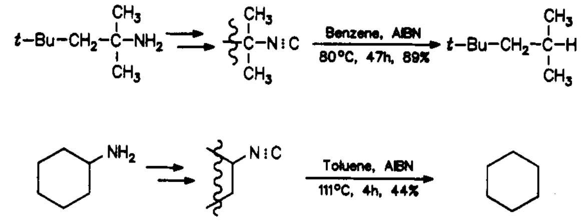
(7)

Dehydroxylation of alcohols under nonacid, mild conditions is one of the major applications of the important Barton-type reactions.[2,11] Our reactive polymer was also effective in transforming cholesterol quantitatively into 5-cholestene, eq 8).[12]



(8)

Another important reaction is the deamination of tertiary[2,14] or secondary amines[2,15] via the isocyanides. With our reactive polymer, the rate is rather low, like in the original cases, but a good yield is obtained at least with the tertiary amine,[9] eq 9.



(9)

In all experiments done so far, the reactive polymer matches completely the reactivity and selectivity of tributyltin hydride[2,3] under mild conditions when some more time[9] for the diffusion into and out of the polymer beads is allowed. Thus, the full advantage of easier processing, of clean and simple workup of the products, of avoiding organotin waste problems, and, last but not least, of regeneration of the reactive polymer for multiple use[9] can be taken.

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Supplementary Material Available: Experimental details for eqs 2–9 (3 pages). Ordering information is given on any current masthead page.

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[9] In a typical procedure, unless stated otherwise in the equations, a suspension or, respectively, solution of 3.0 mmol of the halide, 5.0 g (6.0 mmol Sn–H) of the tin hydride resin,[6] and 0.01 g (0.06 mmol) of AIBN in 25 mL of dry benzene or toluene are slowly stirred, ca. 100 rpm, at 60 °C for 4 h under argon (no magnetic stirring, no direct contact of the stirrer with the wall of the flask, in order to avoid abrasion of the polystyrene beads). The mixture then is filtered—if turbid, through a, e.g., gel filter—and washed with 10 mL of benzene (toluene), the solvent is evaporated under reduced pressure, and the product is dried in vacuo. The yields are 100%, in most cases, of the bromides even after 2 h, and the mp are correct. After 1 h of stirring, the products of bromides are pure in ^{1}H NMR, but the mp are low by 2–3 °C and correct after recrystallization. In eq 7, DMSO is used as solvent. With isocyanides, eq 9, their solution is dropped slowly to the stirred suspension of the hydride resin at the indicated temperature. After the time indicated, the solution has been analyzed by quantitative GLC. Regeneration of the used resin: First, some distannane is split by saturated iodine solution in toluene at rt during 16 h. Then, the resin can be reduced with di-*n*-butylaluminum hydride (5 equiv) in dry THF (ca. 1 M) and washed three times with dry THF. The same regeneration is applied after having carried out eq 8. In the case of the cyanides, eq 9, the resin is treated 16 h with 1.5 volumes of boiling acetyl chloride before reduction as above.

[10] See, for example: Neumann, W. P. *The Organic Chemistry of Tin*; J. Wiley: New York, 1970. Harrison, P. G. *Chemistry of Tin*; Blackie: Glasgow, 1989.

[11] Barton, D. H. R.; Motherwell, W. B. *Pure Appl. Chem.* **1981**, *53*, 15.

[12] This individual reaction has been accepted as a check for the suitability of another reagent, $(Me_3Si)_3SiH$,[13] recommended recently as competitor for Bu_3SnH. It seemed important, therefore, to take the same reaction now in order to test our new reactive polymer.

[13] Schummer, D.; Höfle, G. *Synlett* **1990**, 705.

[14] Barton, D. H. R.; Bringmann, G.; Lamotte, G.; Motherwell, W. B.; Motherwell, R. S. H.; Porter, A. E. A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2657.

[15] Saegusa, T.; Kobayashi, S.; Ito, Y.; Yasuda, N. J. *Am. Chem. Soc.* **1968**, *90*, 4182.