

An Immobilized Organotin Catalyst for Reduction of Ketones and Aldehydes

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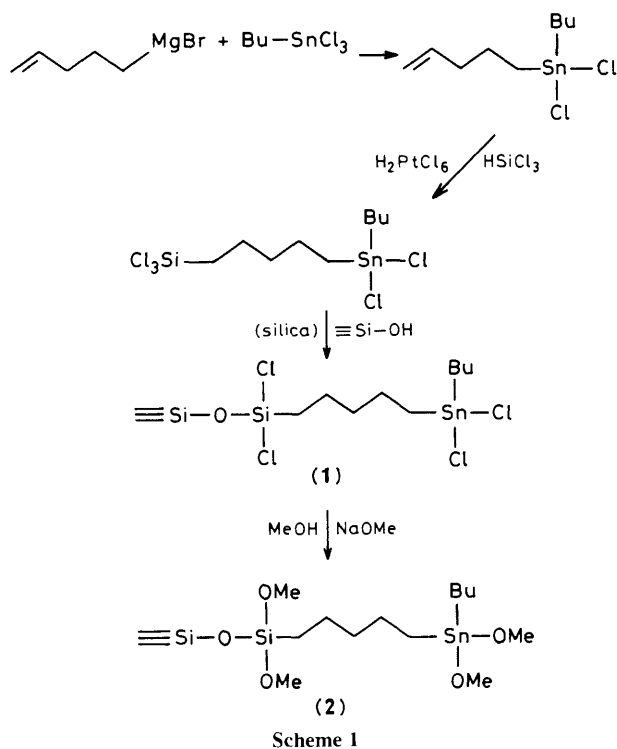
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A dialkyltin dimethoxide linked to the surface of silica functions as an efficient and readily recovered and recycled hydride transfer catalyst for the reduction of ketones and aldehydes using polymethylhydrosiloxane as the hydrogen source.

Although hydrides of main-group elements are outstandingly successful homogeneous reducing agents, they have hitherto received little attention in immobilized forms. An ion exchanger carrying BH_4 groups has been described¹ and an organotin hydride reagent linked to a polymer resin has been prepared.² The latter showed an interesting spectrum of activity as a reducing agent and its activity could be improved by co-addition of PtCl_4 , but the reagent was difficult to regenerate by LiAlH_4 treatment and its activity declined on each cycle. Tributyltin hydride adsorbed on silica has also been examined for the selective reduction of aldehydes.³

Organotin alkoxides are known to function as efficient catalysts for the transfer of hydrogen from silicon hydrides to organic substrates such as carbonyl compounds⁴ and are comparable in their range of applications to the stoichiometric organotin hydride reagents,⁵ which continue to find important applications in organic synthesis.⁶ We have prepared an organotin compound linked to the surface of silica and have developed a convenient, immobilized version of this homogeneous reducing system.

The Grignard reagent prepared from 5-bromopent-1-ene reacted with butyltin trichloride to give butylpent-4-enyltin dichloride[†] which was hydrosilylated⁷ and then treated with Corasil II silica (a low surface area 37–50 μm pellicular silica consisting of non-porous glass spheres with a 1–2 μm layer of silica fused to the surface) as shown in Scheme 1. The



Scheme 1

[†] All new compounds gave satisfactory spectroscopic and microanalytical data.

dichlorostannane (1), having 0.40 mequiv. g^{-1} of organotin groups, was then treated with sodium methoxide in refluxing methanol for 2 h and the resulting solid was exhaustively extracted in a soxhlet apparatus with anhydrous methanol,[‡] yielding a product (2) with 0.25 mequiv. g^{-1} of organotin groups.

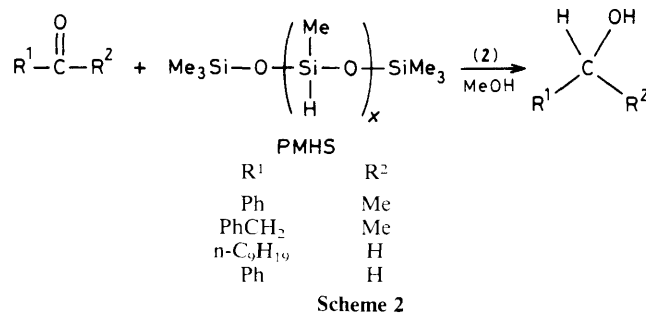
Organosilicon hydrides are particularly attractive sources of hydrogen for tin-mediated reductions, with polymethylhydrosiloxane (PMHS) being an outstanding candidate in view of its availability, ease of handling, and of removal.⁸ When the bonded organotin dichloride phase was refluxed in PMHS containing acetophenone, no reduction of the ketone occurred. Similarly, homogeneous organotin halide catalysts such as dibutyltin dichloride also failed to effect any reduction. However, both the bonded organotin dimethoxide phase (2) and its homogeneous models were active catalysts for the reduction of acetophenone. When a 1 : 5 : 20 w/w/w mixture of phase (2), acetophenone, and PMHS was refluxed in anhydrous methanol, the carbonyl group of the ketone was reduced completely during ca. 48 h (monitored by i.r. spectroscopy) and filtering and subsequent aqueous work-up afforded 1-phenylethanol as the sole product of reaction.

It was demonstrated that the catalyst could be readily recovered and recycled without appreciable loss of activity. Thus, following an acetophenone reduction as above, the catalyst was filtered off under a dry atmosphere, washed with anhydrous methanol and added to a fresh, refluxing mixture of acetophenone and PMHS in methanol. Reduction again occurred within 48 h. A batch of catalyst was similarly cycled through four consecutive reduction sequences without any noticeable lowering of activity.

In a further series of experiments the reductions of *n*-decanal, benzaldehyde, and benzyl methyl ketone were also effected smoothly with the immobilized catalyst (2) and PMHS in refluxing methanol (Scheme 2). The ketone was reduced at about the same rate as acetophenone, whereas the reductions of the aldehydes were appreciably (5–10 times) faster, benzaldehyde giving the fastest rate of all. Thus, the new catalyst also shows promise of useful selectivity in the reduction of polycarbonyl compounds.

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Scheme 2

[‡] Failure to remove all of the NaOMe results in subsequent polymerization of the PMHS.

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