

Recommended Work-up Procedure for Reductions Employing Tri-*n*-butyltin Hydride

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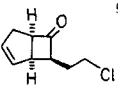
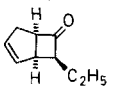
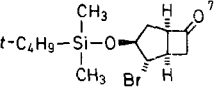
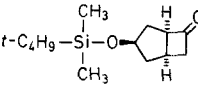
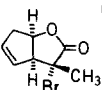
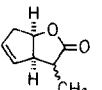
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Tri-*n*-butyltin hydride is an excellent reagent for the hydrodehalogenation of alkyl halides¹. However, a major drawback in employing this reagent can be the separation of the product(s) from the tin residues, particularly when excess of the hydride is used to elevate the rate of reduction. In addition, chromatographic separations performed over silica may lead to unwanted side reactions².

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Table. Reduction of Some Alkyl Halides using Tri-*n*-butyltin Hydride

Substrate (Ref.)	Product ^a	Reaction time	Equiv of tri- <i>n</i> -butyltin hydride	Yield ^b [%]	b.p./torr	Lit. b.p./torr
1 ⁴	2	10 h	10	80	90°/0.1	90°/0.1 ⁴
		90 h	8	65	115°/11	130°/30 ⁶
		20 h	5	60	130°/15	— ^c
		90 h	10	70	130°/11	— ^d
$\text{C}_6\text{H}_5\text{—C(=O)—CH}_2\text{—Br}$	$\text{C}_6\text{H}_5\text{—C(=O)—CH}_3$	90 h	5	92	—	—

^a Compounds distilled using the Kugelrohr (bulb-to-bulb) system; temperatures quoted are oven temperatures at distillation.

^b Yields refer to isolated distilled samples.

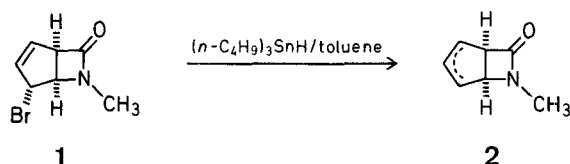
^c $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$ calc. C 64.94 H 10.06
(240.4) found 64.9 10.1
I.R. (film): $\nu_{\text{max}} = 1780\text{ cm}^{-1}$.

^d $\text{C}_8\text{H}_{10}\text{O}_2$ (138.1): M.S.: $m/e = 138.0679$, calc. 138.0679 (M^+).
I.R. (film): $\nu_{\text{max}} = 1760\text{ cm}^{-1}$.

One solution to the problem involves the use of a small amount of tin hydride together with sodium borohydride to recycle the tin halide produced³. Obviously this method is only applicable to halogenated substrates which are otherwise inert to sodium borohydride.

Herein we report an alternative solution to the problem, namely a simple work-up procedure which separates the tin halide and unreacted tin hydride from the desired product. Our method depends upon (a) the mutual insolubility of hexane and acetonitrile (b) the pronounced solubility of tri-*n*-butyltin species in hexane, and (c) the preferential partition of other organic molecules into acetonitrile in the acetonitrile-hexane two phase system.

We have applied the procedure to a variety of substrates (e.g. **1**) (Table) and the yields of reduced products (e.g. **2**) (which are not optimized) range from good to excellent. In all cases, the structures of the products were established by comparison of N.M.R. and T.L.C. data (petroleum ether/ethyl acetate elution over silica) with those from authentic samples. These data indicated also that the reaction products suffered little (<5%) if any contamination by tin residues.



Procedure for the Reduction of Alkyl Halides using Tri-*n*-butyltin Hydride:

The alkyl halide (0.1–0.5 g) is heated under reflux in toluene (and a suitable cosolvent if necessary) containing tri-*n*-butyltin hydride

(5–10 mol equiv) for 10–90 h. The toluene (and any cosolvent) is removed in vacuo and the residue is dissolved in acetonitrile (10 ml). This solution is washed with dry hexane (5 × 10 ml) and evaporated to yield the corresponding reduction product essentially free of tin residues. The product is purified by Kugelrohr distillation (Table).

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