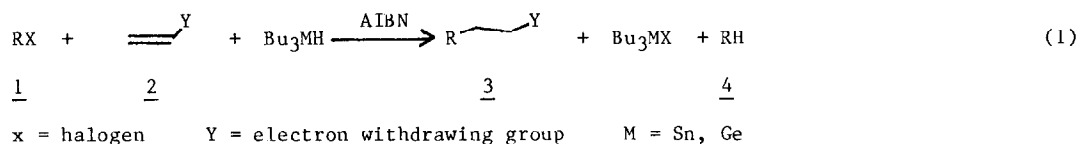


ALKYL ADDITIONS TO ACTIVE OLEFINS BY
 TRIBUTYLGERMANIUM HYDRIDE REDUCTION OF ALKYL HALIDES

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ABSTRACT: Tri(n-butyl)germanium hydride is a superior reagent for the reductive addition of alkyl halides to active olefins.

The intermolecular addition of alkyls to active olefins by the tri(n-butyl)tin hydride reduction of alkyl halides has recently been employed by several groups.¹⁻³ The utility of reaction 1 (M = Sn) is apparently limited to terminal olefins, which must be employed in



five- to ten-fold molar excess. The use of stoichiometric amounts of olefins results in formation of RH, the simple reduction product from RX, in significant amounts.²

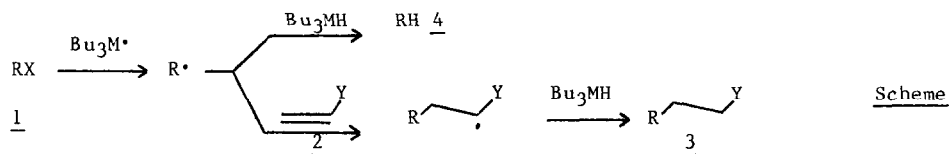
We wish to report that tri-(n-butyl)germanium hydride is a superior reagent for reaction 1 in cases where competing production of RH is a problem. Indeed, fair to good yields of the addition product can often be obtained by employing near-stoichiometric quantities of the olefin.

Table I

<u>1</u>	<u>2</u>	<u>M</u>	<u>Solvent</u>	<u>3(%)</u>	<u>4(%)</u>
<u>n</u> -C ₁₁ H ₂₃ I	a	Ge	CH ₃ CN	71	11
<u>n</u> -C ₁₁ H ₂₃ I	a	Ge	C ₆ H ₆	63	14
<u>n</u> -C ₁₁ H ₂₃ I	a	Sn	C ₆ H ₆	40	47
PhCH ₂ I	a	Ge	C ₆ H ₆	76	--
PhCH ₂ I	a	Sn	C ₆ H ₆	33	--
<u>n</u> -C ₁₁ H ₂₃ I	b	Ge	CH ₃ CN	21	60
<u>n</u> -C ₁₁ H ₂₃ I	b	Sn	C ₆ H ₆	5	95
<u>c</u> -C ₆ H ₁₁ I	b	Ge	CH ₃ CN	31	--
<u>c</u> -C ₆ H ₁₁ I	b	Sn	C ₆ H ₆	7	--

The results summarized in Table I reveal the advantages as well as the limitations of the germyl hydride reagent. In a typical experiment the alkyl halide (0.5 mmol), the olefin (2a = acrylonitrile, 2b = 2-cyclohexen-1-one; 0.75 mmol), the metal hydride (0.5 mmol), and AIBN (azobis[isobutyronitrile], 0.1 mmol) were dissolved in 5 ml of deoxygenated solvent. The solution was warmed to reflux 6-12 h. The percent yields of 3 and 4 in Table I, based upon RX, were determined by GLC using an internal standard. GLC response factors were established using authentic samples of 3 and 4. The yield of 4 could not be determined for RH = cyclohexane, toluene due to chromatographic interference from the solvent. Benzene was the solvent of choice for M = Sn. Acetonitrile gave comparable or slightly improved yields for M = Ge.

The improved yields using tributylgermanium hydride presumably arise from the lower reactivity of germyl hydrides relative to stannyl hydrides towards alkyl radicals.⁵ As illustrated in the Scheme, product 4 results from hydrogen transfer to R• prior to the interception of R• by the active olefin. Poor yields of 3 were obtained, even with tributylgermanium hydride, when



the olefin was 2-cyclohexene-1-one. The rate of alkyl radical addition to internal olefins is apparently too sluggish to permit efficient production of 3. When 1-iodoundecane was reduced by tributylgermanium hydride in the presence of a tenfold excess of 2-cyclohexen-1-one, 3-undecylcyclohexan-1-one was obtained in 68% yield. Clearly there is a need for metal hydrides of appropriate reactivity to permit the use of interesting olefins, such as hindered α,β -unsaturated ketones, in stoichiometric quantities. Research towards this goal is in progress.

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