

Table 3. Competitive Transport of Butylammonium Perchlorates^a

Carriers	Transport rates $\times 10^5$ mol/hr			
	<i>n</i> -Bu	<i>iso</i> -Bu	<i>sec</i> -Bu	<i>tert</i> -Bu
2	17.2	9.01	4.17	0.24
DB18C6	10.4	6.25	5.42	3.83

^aSource Phase: Contains all four butylammonium perchlorates (each in 0.50 mmol/5.0 mL D₂O); membrane phase: carrier (0.05 mmol/15 mL CDCl₃); receiving phase: 5.0 mL D₂O. After 24 hrs of stirring the total transported guests were measured by Orion lonalyzer 901 using a perchlorate ion-selective electrode and individual guests were determined by ¹H-NMR spectrometer (500 MHz), respectively.

the complexation occurs in the central part of crown periphery and significant conformational reorganization of the calixarene moiety was induced upon complexation with butylammonium guests.

To understand the molecular recognition properties of calix-crown ligands better, we performed competitive transport from the mixture containing all four butylammonium perchlorates through chloroform liquid membrane using U-tube at 25°C. After constant stirring of organic membrane layer for 24 hrs, the receiving phase was removed and the amount of transported butylammonium guests were determined by ¹H-NMR spectroscopy (Table 3). For the sake of detectability and convenience, deuterated solvents (D₂O and CDCl₃) were used for the constituents of liquid membrane. The transport efficiency of **2** for the varying structures of butylamine decreases in the order *n*-Bu > *iso*-Bu > *sec*-Bu > *tert*-Bu. This order is in good agreement with the result of extraction experiments. Meanwhile the discrimination characteristics between *n*-Bu, *iso*-Bu and *sec*-Bu guests is moderate, the remarkably enhanced discrimination behavior between *n*-Bu and *tert*-Bu guests was observed. The selectivity in transport between *n*-butyl and *tert*-butylammonium salts is over 70-fold compared to the value of 2.70 for DB18C6.

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5-(π -Endo)-exo Vinyl Radical Cyclization Mediated by the Addition of Stannyl Radicals to Triple Bonds

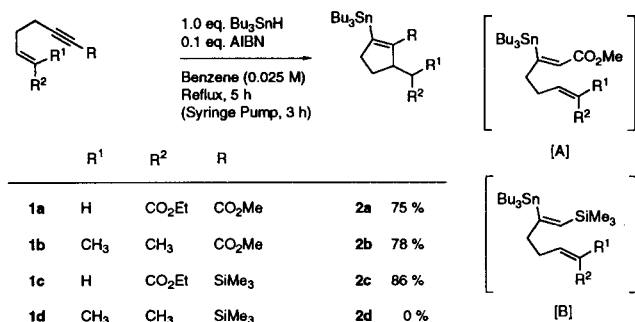
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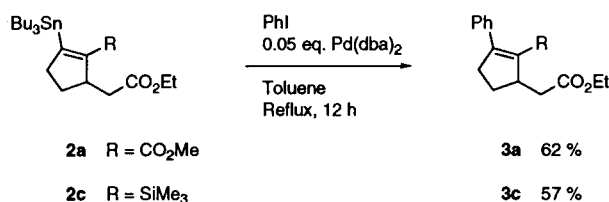
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Vinyl radical cyclization reactions can be subdivided into two classes; those in which the π -system of the vinyl radical is exocyclic to the ring formed and those in which it is endocyclic to the ring. These may be called as (π -exo) and (π -endo) type cyclizations.¹ Examples abound in each category when vinyl halides are used as substrates.^{2,3} On the other hand, the usefulness of β -stannylvinyl radicals, formed by the addition of stannyl radicals to triple bonds, is manifested mainly by (π -exo) type cyclizations.⁴ In each case, the reaction is initiated by the addition of a stannyl radical to the terminal carbon of the terminal triple bond. (π -Endo) type cyclizations of β -stannylvinyl radicals were used much less frequently,^{4a} presumably due to the regioselectivity problem in reversible addition of stannyl radicals to internal triple bonds. We now wish to report here examples of (π -endo) cyclization of β -stannylvinyl radicals generated regioselectively from methoxycarbonyl- and trimethylsilyl-substituted alkynes.

The substrates **1a** and **1b** were converted into stannylcyclopentene derivatives **2a** and **2b** in reasonably good yields. The cyclization reactions are considered to proceed through the α -methoxycarbonyl- β -stannylvinyl radicals [A] in which the σ -vinyl radical (the semioccupied orbital is orthogonal



Scheme 1.



Scheme 2.

to the π -system) is inductively influenced by both α -carbonyl and β -stannyl substituents and reactive towards both electron-poor and electron-rich double bonds. This behavior is not surprising in view of the results on (π -*exo*) type cyclizations of α -carbonyl- β -stannylvinyl radicals generated from propiolates and acetylenic ketones.⁵

The substrate **1c** was converted into the product **2c** in good yield, but the substrate **1d** was recovered in high yield under identical reaction conditions. From the results, we can surmise that α -silyl- β -stannylvinyl radicals [B] are nucleophilic in nature (with high SOMO energy) and react only with electron-deficient double bonds.

The above reactions afford cyclopentene derivatives with multiple substituents, useful for further manipulations. For example, palladium-catalyzed arylation of **2a** and **2c** afforded products **3a** and **3c** in reasonable yields (Scheme 2).

The reactivity profile of substituted vinyl radicals delineated here for (π -*endo*) type cyclizations will be used as a guide in cyclopentenoid synthesis.

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Facile Reduction of Aryl Halides with Borohydride Exchange Resin-Nickel Acetate

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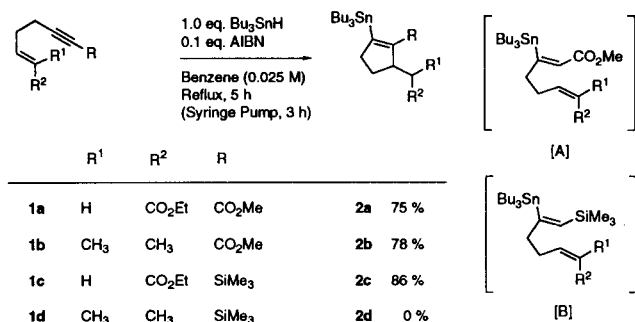
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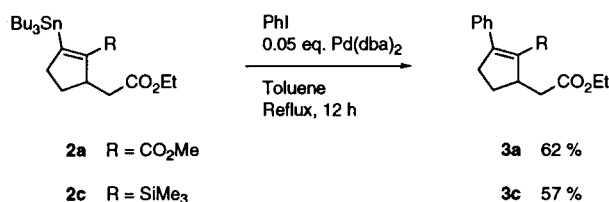
The combination of sodium borohydride with transition metal salts exhibits enhanced reducing abilities when compared with sodium borohydride itself.¹ Thus NaBH₄-Pd/C² or NaBH₄-PdCl₂^{3,4} and more recently NaBH₄-CuCl₂⁵ have been reported to be useful for the dehalogenation of aryl halides in alcoholic solvents. NaBH₄-[Ni(0)(Ph₃P)₃] in DMF⁶ was also reported to be effective in the hydrogenolysis of aryl bromides.

Sometime ago, borohydride exchange resin (BER) was introduced by Gibson and Bailly⁷ and we reported BER is an interesting chemoselective reducing agent for carbonyl compounds in alcoholic solvents^{8,9} and several other significant applications were also presented.¹⁰ Recently we have found that BER is much more stable than NaBH₄ in methanol in the presence of nickel boride, and BER-Ni(OAc)₂ in methanol proved to be an excellent reduction system for nitro compounds.¹¹ We also found that both 4-bromonitrobenzene and 4-chloronitrobenzene were quantitatively reduced to aniline in methanol in 1 h at room temperature. This prompted us to explore the generality of the dehalogenation with BER-Ni(OAc)₂. In this paper, we wish to report that BER-Ni(OAc)₂ system is capable of reducing aryl halides in excellent yield with good selectivity.

The procedure is very simple. Aryl halide was added to the mixture of BER (5 mol equiv) and Ni(OAc)₂ (0.5 mol equiv) in methanol. The reaction mixture was then stirred at room temperature or under reflux for 1-3 h. After the reaction was completed, the resin was filtered and methanol was evaporated under reduced pressure to give the nearly pure product. The product was purified by silica gel column



Scheme 1.



Scheme 2.

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