



Figure 4
Competing mechanistic pathways for reaction of II with Bu₃SnH.

equiv) and *p*-dimethoxybenzene (0.1–0.2 equiv, internal standard) were added. The resulting mixture was rapidly heated to reflux and the progress of the reaction was followed by GC until no further consumption of starting material was observed. Product yields and ratios were then determined by GC and ¹H NMR analyses. The results of the two analyses were comparable (typically ± 5%), and only the GC results are shown in the Tables. The complete data set is contained in the Additional Material.

The results of single experiments for the cyclization of enol carbonate 11b at 0.1 M, 0.01 M and 0.001 M are summarized in the upper part of Table 1 (entries 1–3). At the higher two concentrations, complete conversion of 11b was observed and reduced product 14b was formed in good yield. None of the directly reduced product 18b was observed even at the highest concentration, indicating that the intermediate radical cyclization is fast ($k_c > 10^6 \text{ s}^{-1}$). Negligible amounts of ketone 15 ($\leq 2\%$) were observed, and its yields were not dependent on the tin hydride concentration. Accordingly, no evidence was obtained for fragmentation of intermediate α -alkoxycarbonyloxy radical 13b. At the lowest tin hydride concentration (entry 3), the conversion stopped with 25% of the starting iodide remaining, but again only a trace of 15 (1%) was detected. These results suggest chain propagation problems at this concentration, which is near the dilution limit for typical radical chain reactions.

The results for cyclization of enol acetate 11a at four different concentrations are shown in the lower part of Table 1 (entries 4–7). Since increased amounts of ketone 15

Table 1: Product Ratios in Bu₃SnH Mediated Cyclizations of IIa,b^a

Entry	Precursor	[Bu ₃ SnH]	Yld ^b 14a,b	Yld ^b 15a,b	Recovered ^b 13a,b	Total Yld
1	11b ^c	0.1 M	80%	2%	-	82%
2	11b ^c	0.01 M	70%	1%	-	71%
3	11b ^c	0.001 M	60%	1%	25%	86%
4	11a ^d	0.1 M	95%	2%	-	97%
5	11a ^d	0.01 M	73%	8%	-	81%
6	11a ^d	0.005 M	28%	16%	42%	86%
7	11a ^d	0.001 M	1%	16%	43%	60%

a) C₆H₆ or C₆D₆, 80°C, b) GC yield against *p*-dimethoxybenzene standard; 2-3/1 mixture of stereoisomers, c) single experiment, d) average of three experiments.