imines by H. Yamamoto,[13] *cis*-isomer was obtained as major product.

We turned our attention to other *trans*-selective reduction approach for the hydroxy-imine **7**. The reduction of the imine **7** with $NaBH(OAc)_3$, which is useful for the "directed reduction",[14] however, gave almost an equal amount of both isomers. Hydrogenation of the imine **7** with PtO_2 as catalyst also gave the *cis*-isomer as major product[15] (Table 2).

In conclusion, nucleophilic additions of sterically hindered carbon nucleophiles to the activated lactam **3** can be efficiently carried out through organocerium complexes. Also, the stereoselective reduction of five-membered cyclic imine **6** and **7** has been done with several reagents. Although a further study is necessary to develop an efficient *trans*-selective reduction method, our results will be useful for the preparation of *cis*-2,5-disubstituted pyrrolidine derivatives. A synthetic application of this work is in progress.

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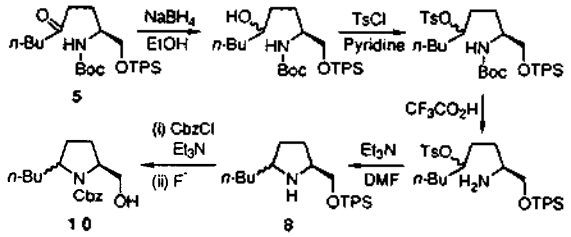
9. In the case of **6** (R=*i*-Pr), a similar selectivity was observed.
10. It was difficult to separate *cis*-**8** and *trans*-**8** mixture by column chromatography; however, almost 1 : 1 ratio of *cis/trans* could be determined by ^1H NMR spectrum analysis. If desired, each isomer can be separated at the stage of **10** by careful column chromatography on SiO_2.



5 8 10

11. It has been assumed that the catalytic reductions of 2,5-disubstituted cyclic imines produce the major *cis*-pyrrolidines: see the paper of D. Bacos *et al.* in reference 1.
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Stabilizing Effect of Tributyltin Group on Adjacent Carbon Radicals

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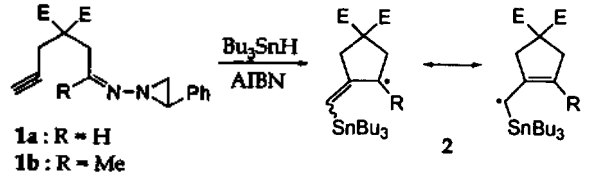
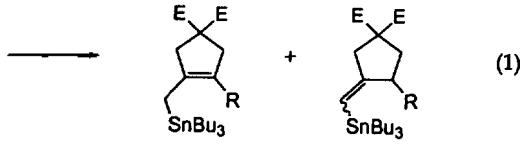
In connection with radical cyclization of N-aziridinylimines,[1,2] we have reported that the radical cyclization of **1** afforded only **3** in high yields without the formation of **4** (eq. 1), while **5** gave a 87 : 13 mixture of **6** and **7** under the similar radical conditions due to the formation of an intermediate allylic radical (eq. 2). Further studies with **8** gave the similar results and only **9a** and **9b** were isolated in 82% and 89% yield, respectively (eq. 3).[3,4] It is also noteworthy that 1,5-hydrogen transfer did not take place prior to radical cyclization. Since the reaction should proceed via an intermediacy of **2**, the sole formation of **3** and **9** was quite surprising to us. We assumed that the reason for this observation could

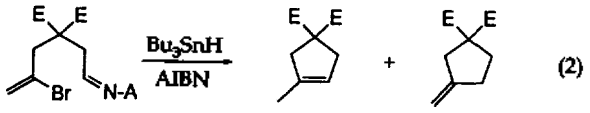
be due to the stabilizing effect of tributyltin group on adjacent carbon radicals.



1a : R = H
1b : R = Me

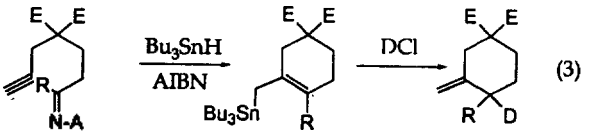


3a : 84%
3b : 96% (100:0) **4** (1)



5
A=2-Phenyl-N-aziridinyl

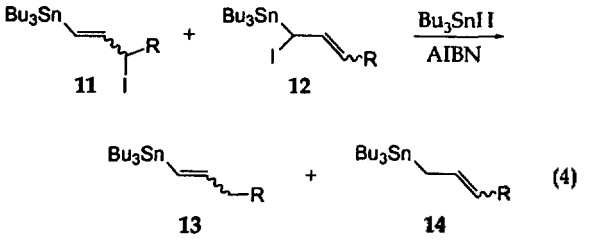
6 (87:13) **7** (2)



8a : R = H
8b : R = Me

9a : 82%
9b : 89%

10 (3)



11 **12**

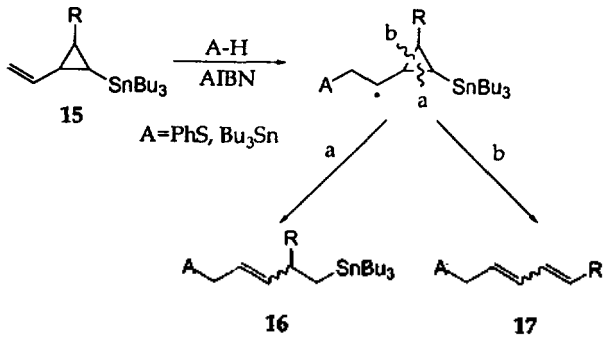
13 **14** (4)

a : R=H, **11a**/**12a**=1/2, **13a**/**14a**=1/1, **13a**+**14a**=94%

b : R=Me, **11b**/**12b**=1/10, **13b**/**14b**=1/1, **13b**+**14b**=86%

We were encouraged to apply our finding to the preparation of allyltin compounds. However, treatment of a 1 : 1 mixture of **11a** and **12a** with Bu_3SnH (1.1 equiv) and AIBN (0.1 equiv) in refluxing benzene for 2h did not give **14a** as a sole product, and instead gave a 1 : 1 mixture of **13a** and **14a** in 94% yield (eq. 4). A similar result was also obtained with a mixture of **11b** and **12b**. It is evident that the tributyltin group did not affect the regiochemical outcome when the tributyltin substituted acyclic allyl radical reacted with Bu_3SnH. At the present time, we offer no explanations as to why the discrepancy was observed in the reaction.

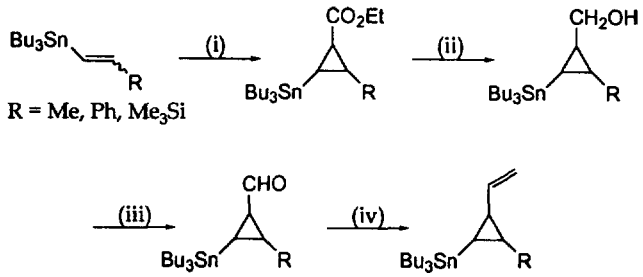
Both α-sily and β-silyl substituents have been known to stabilize alkyl radicals.[5] Miura *et al* studied the stabilizing effect of the α-trialkylsilyl group on adjacent carbon radicals using radical induced ring opening of 1-trialkylsilylvinylcyclopropanes.[6] Although the α-stannyl substituent has been suggested to stabilize alkyl radicals to some extent,[7] no direct evidence has been reported. Thus, we examined the stabilizing effect of the tributyltin group on adjacent carbon-centered radicals using radical induced ring opening of tributyltin substituted vinylcyclopropanes. As shown in Scheme 1, the stabilizing effect of tributyltin group would give rise to cleavage a to yield **16**, although the bond cleavage depends critically on the nature of the R group.



15
A=PhS, Bu_3Sn

16 **17**

Scheme 1.



R = Me, Ph, Me_3Si

(i) N_2CHCO_2Et, $Pd(OAc)_2$ (ii) $LiAlH_4$
(iii) $(COCl)_2$/DMSO/Et_3N (iv) $Ph_3P{=}CH_2$

Scheme 2.

Table 1. Radical induced ring opening of tributyltin substituted vinylcyclopropanes[a]

Substate	A-H	Yield (16+17), 16/17
15a: R=H	PhSH	66%, 95/5
15b: R=Me	PhSH	76%, 75/25
15c: R=Ph	Bu_3SnH	70%, 0/100
15d: R=Me_3Si	PhSH	40%, 33/67

[a] The stereochemistry of **15** has not been determined and stereoisomeric mixtures were used.

The model compounds chosen for this study were tributyltin subsituted vinylcyclopropanes (**15**) which were prepared by the routine operations. **15a** was prepared from 2-3-tributylstannyl-2-propen-1-ol by a three-step sequence[9] and vinyl cyclopropanes (**15b**, **15c**, **15d**) were prepared as shown in Scheme 2. The stereochemistry of vinylcyclopropanes (**15b**, **15c**, **15d**) could not be determined by ^1H NMR and stereoisomeric mixtures of **15** were utilized in the radical reaction.

Treatment of **15a** with thiophenol (1.2 equiv) and AIBN (0.1 equiv) in refluxing benzene for 3h gave a 95 : 5 mixture of **16a** and **17a** in 66% yield, suggesting that the tributyltin group should stabilize an adjacent carbon-centered radical. As shown in Table 1, radical reaction of **15b** under the simi-

lar conditions gave a 75 : 25 mixture of **16b** and **17b** in 76% yield. Since α-alkyl substituent is known to stabilize the adjacent carbon radical by *ca.* 3 kcal/mol,[9] the stabilizing effect of α-tributyltin group could be somewhat higher than this magnitude. When **15c** was treated with thiophenol and AIBN in refluxing benzene, the product formed decomposed during silica gel column chromatographic separation. Therefore, **15c** was treated with Bu_3SnH and AIBN in refluxing benzene for 4 h and only **17c** was isolated without the formation of **16c**, indicating that the stabilizing effect of α-tributyltin group should be far less than that of α-phenyl group. Finally, our affention was given to a competitive study between tributyltin group and trimethylsilyl group. When **15d** was treated with thiophenol and AIBN in refluxing benzene for 3 h, a 33 : 67 mixture of **16d** and **17d** was obtained in 40% yield. The result obtained in this study suggests that the stabilizing effect of α-tributyltin group seems to be slightly less than that of α-trimethylsilyl group and the general order for stabilizing adjacent carbon radicals woud be $Ph > Me_3Si > Bu_3Sn > alkyl$.

Acknowledgment. We gratefully acknowledge the financial support of the Organic Chemistry Research Center (KOSEF).

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3. Treatment of **9** with deuterochloride in dichloromethane at room temperature for 0.5 h gave **10** in essentially quantitative yields.
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Synthetic Studies on Liposidomycins: Synthesis of 5-Aminopentose Moiety

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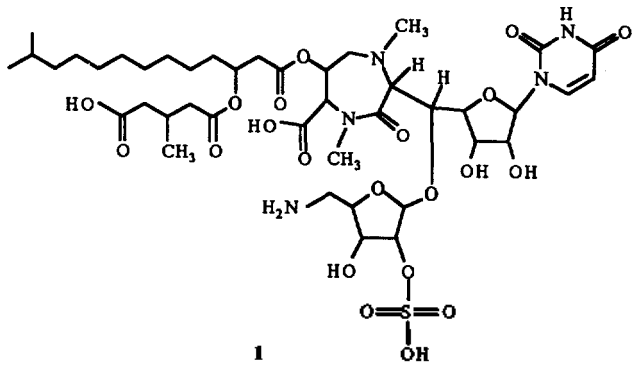
The liposidomycins are a family of novel lipid-containing nucleoside antibiotics of unusual complexity, recently found in the culture filtrate and mycelia of *Streptomyces griseosporeus*,[1] which inhibit formation of the lipid intermediate in peptidoglycan synthesis.[1,2] The primary site of action of liposidomycin C was found to be phospho-MurNAc-pentapeptide transferase, the first step of the peptidoglycan synthesis in the cell wall of *E. coli.* Y-10.[3] The structures of liposidomycins A,[4] B (**1**),[2] and C[2] were proposed on the basis of degradation and spectroscopic studies; their structures are identical except lipid parts. The overall structure of liposidomycins as well as structural components, namely, a diazepinone and a 5-aminopentose 2-sulfate is unique. The present communication reports the synthetic studies of the 5-amino-β-D-ribo-



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furanoside part of liposidomycins. There are a few points to be considered in the planning the synthesis; (i) introduction of the properly protected amino group at C-5, (ii) selective protection of 3-OH and sulfation of 2-OH, and (iii) β-glycosylation.

Diol **3** obtained by hydrolysis of isopropylidene group of compound **2** was transformed into 2,3-O-stannylene sugar **4** in almost quantitative yield by treatment with dibutyltin oxide in refluxing methanol. Reaction of **4** with benzyl bromide in the presence of one equivalent of tetrabutylammonium bromide in refluxing toluene gave a 1 : 1 mixture of 5-bromo-2-O-benzyl ether **5**[5] and 5-bromo-3-O-benzyl ether **6**[6] in 68% yield and no dibenzyl ether was found. In the absence of tertrabutylammonium bromide, the bromination at C-5 did not occur and the benzylation was sluggish. Assignment of **5** and **6** was made on the basis of the 2D ^1H NMR NOESY spectroscopic data: NOE's were observed between methyl protons of the methoxy group and aromatic protons and between the anomeric proton and benzylic protons of the benzyl group in compound **5**. The ^1H NMR chemical shifts and coupling patterns of H-2 and H-3 of acetyl derivatives **10**[7] and **11**[8] further confirmed the assignment