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

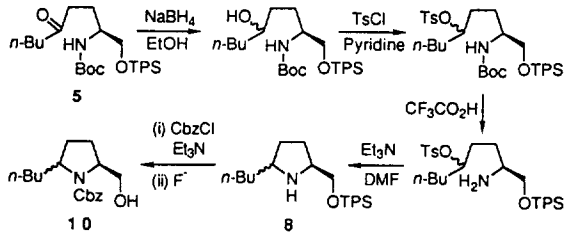
We turned our attention to other *trans*-selective reduction approach for the hydroxy-imine **7**. The reduction of the imine **7** with $NaBH(OAc)_3$, which is useful for the "directed reduction",[14] however, gave almost an equal amount of both isomers. Hydrogenation of the imine **7** with PtO_2 as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

Acknowledgment. This work was supported by Research Institute of Science & Technology, Pohang, 1993.

References

1. (a) Jones, T. H.; Blum, M. S.; Fales, H. M. *Tetrahedron* **1982**, *38*, 1949. (b) Daly, J. W.; Spande, T. F.; Whittaker, N.; Highet, R. J.; Feigl, D.; Nishimori, N.; Tokujama, T.; Myers, C. W. *J. Nat. Prod.* **1986**, *49*, 265. (c) Langlois, N.; Andriamialisoa, R. Z. *Tetrahedron Lett.* **1988**, *29*, 3259. (d) Bacos, D.; Basselier, J. J.; Célérier, J. P.; Lange, C.; Marx, E.; Lhommet, G.; Escoubas, P.; Lemaire, M.; Clément, J. L. *Tetrahedron Lett.* **1988**, *29*, 3061. (e) Jones, T. H.; Blum, M. S.; Escoubas, P.; Musthak Ali, T. M. *J. Nat. Prod.* **1989**, *52*, 779. (f) Bacos, D.; Célérier, J. P.; Marx, E.; Rosset, S.; Lhommet, G. *J. Heterocyclic Chem.* **1990**, *27*, 1387.
2. (a) Kawanami, Y.; Ito, Y.; Kitagawa, T.; Taniguchi, Y.; Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1984**, *25*, 857. (b) Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1977**, *42*, 1663. (c) For a review, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
3. (a) Machinaga, N.; Kibayashi, C. *Tetrahedron Lett.* **1990**, *31*, 3637. (b) Yamamoto, Y.; Ohmori, H.; Sawada, S. *Synlett*, **1991**, 319. (c) Marzi, M.; Minetti, P.; Misiti, D. *Tetrahedron*, **1992**, *48*, 10127. (d) Dumas, F.; d'Angelo, J. *Tetrahedron Lett.* **1992**, *33*, 2005. (e) Langlois, N.; Rojas, A. *Tetrahedron*, **1993**, *49*, 77. (f) Yuasa, Y.; Ando, J.; Shibuja, S. *J. Chem. Soc., Chem Commun.* **1994**, 455. (g) Higashijama, K.; Inoue, H.; Takahashi, H. *Tetrahedron* **1994**, *50*, 1083. (h) Janowitz, A.; Vavrecka, M.; Hesse, M. *Helv. Chim. Acta* **1991**, *74*, 1352.
4. Silverman, R. B.; Levy, M. A. *J. Org. Chem.* **1980**, *45*, 815. The (*S*)-form is commercially available from Aldrich.
5. Hwang, Y. C.; Chu, M.; Fowler, F. W. *J. Org. Chem.* **1985**, *50*, 3885.
6. Ohta, T.; Hosoi, A.; Kimura, T.; Nozoe, S. *Chem. Lett.* **1987**, 2091.
7. (a) Imamoto, T.; Kusumoto, T.; Yokoyama, M. *J. Chem. Soc., Chem. Comm.* **1982**, 1042. (b) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392, and references cited therein.
8. Giovannini, A.; Savoia, D.; Umani-Ronchi, A. *J. Org. Chem.* **1989**, *54*, 228.
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.



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.
12. (a) Marco, J. L. *J. Heterocyclic Chem.* **1986**. *23*, 1059. (b) Hill, R. K.; Chan, T.-H. *Tetrahedron* **1965**, *21*, 2019.
13. Maruoka, K.; Miyazaki, T.; Ando, M.; Matsumura, Y.; Sakane, S.; Hattori, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 2831.
14. (a) Saksena, A. K.; Mangiaracina, P. *Tetrahedron Lett.* **1983**, *24*, 273. (b) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560, and references cited therein.
15. An attempted directed hydrogenation [$ClRh(PPh_3)_3$, *t*-BuOK, 60 psi H_2, THF, 25 ℃, 24 h] was not successful: Thompson, H. W.; McPherson, E. *J. Am. Chem. Soc.* **1974**, *96*, 6232. For a review of the directed hydrogenation, see: Brown, J. M. *Angew. Chem. Int. Ed.* **1987**, *26*, 190.

Stabilizing Effect of Tributyltin Group on Adjacent Carbon Radicals

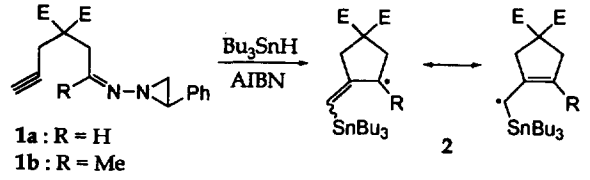
Sunggak Kim* and Kyeong Mog Lee

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

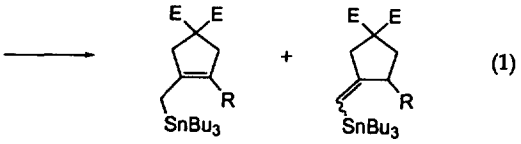
Received July 18, 1994

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.

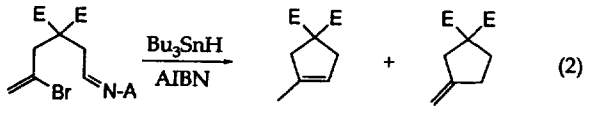


1a : R = H
1b : R = Me



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

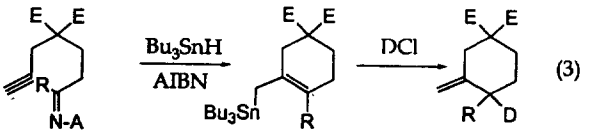
(1)



5
A=2-Phenyl-N-aziridinyl

6 (87:13) **7**

(2)

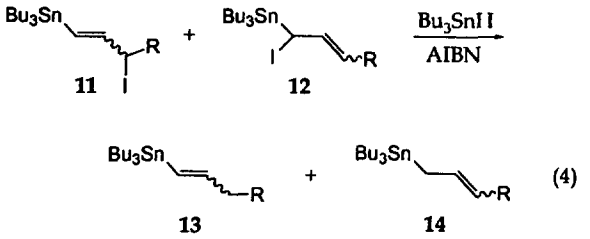


8a : R = H
8b : R = Me

9a : 82%
9b : 89%

10

(3)



11 **12**

13 **14**

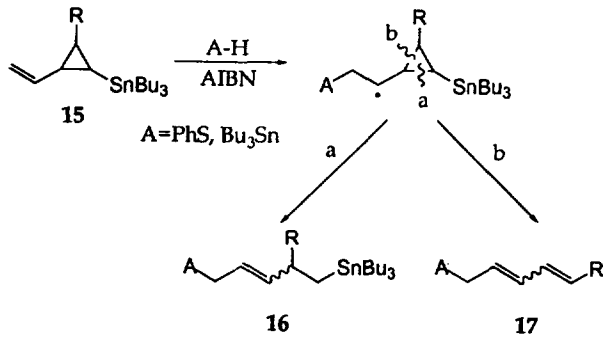
(4)

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.

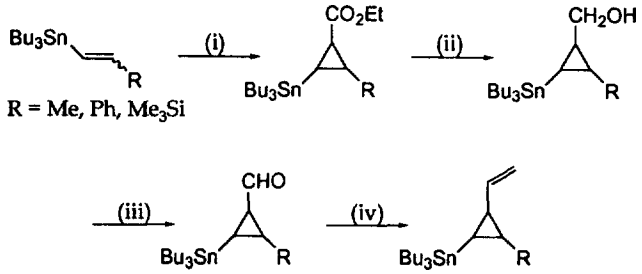
Both α-sily and β-silyl substituents have been known to stabilize alkyl radicals.[5] Miura *et al* studied the stabilizing effect of the α-trialkylsilyl group on adjacent carbon radicals using radical induced ring opening of 1-trialkylsilylvinylcyclopropanes.[6] Although the α-stannyl substituent has 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 Z-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).

References

1. Kim, S.; Kee, I. S.; Lee, S. *J. Am. Chem. Soc.* **1991**, *113*, 9882.
2. Kim, S.; Kee, I. S. *Tetrahedron Lett.* **1993**, *34*, 4213.
3. Treatment of **9** with deuterochloride in dichloromethane at room temperature for 0.5 h gave **10** in essentially quantitative yields.
4. (a) The similar result was also obtained during the studies on 1, *n*-transfer of Bu_3Sn group. Kim, S.; Lim, K. M. *Tetrahedron Lett.* **1993**, *34*, 4851. (b) Kim, S.; Lim, K. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1152.
5. (a) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. (b) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazram, A. S. *J. Am. Chem. Soc.*, **1985**, *107*, 208. (c) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Orgnometallics.* **1987**, **6**, 644.
6. Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1989**, **30**, 4413.
7. Negishi, E-I.; In *Organometallics in Organic Synthesis*; John Wiley: New York. U. S. A., 1980; p 398.
8. (i) CH_2I_2/I_2 Zn-Cu/DME/$(i\text{-}Pr)_2NEt$, 60%, (ii) $(COCl)_2$/DMSO/Et_3N, 95%, (iii) $Ph_3P{=}CH_2$ 80%.
9. Laird, E. R.; Jorgensen, W. L. *J. Org. Chem.* **1990**, *55*, 9.

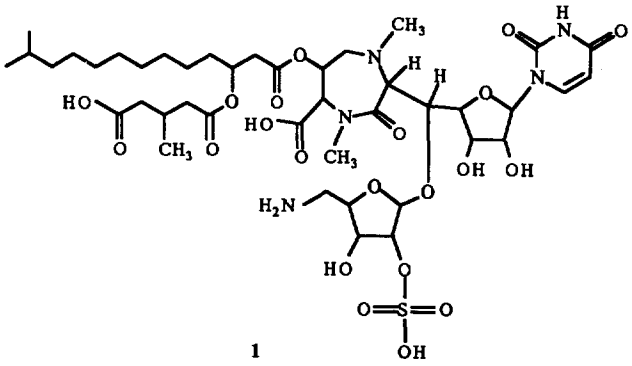
Synthetic Studies on Liposidomycins: Synthesis of 5-Aminopentose Moiety

Kwan Soo Kim*, Yeong Hee Ahn, Eun Young Hurh, Kun Tai Kim, and Yung Hyup Joo

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

Received July 25, 1994

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-



1

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