by a predoctoral grant from the NSF. Additional support was generously provided by Hoffmann-La Roche, ICI Pharmaceuticals, Bristol-Myers Squibb, Pfizer, and Hewlett-Packard.

Supplementary Material Available: Detailed experimental procedures for TDI-G footprinting and autoradiogram of nondenaturing PAGE gel used in separation of protein-bound from unbound DNA (8 pages). Ordering information is given on any current masthead page.

Radical Reactions of Vinyl Epoxides via Radical Translocations by a Novel 1,5-*n*-Bu$_3$Sn Group or a 1,5-Hydrogen-Atom Transfer

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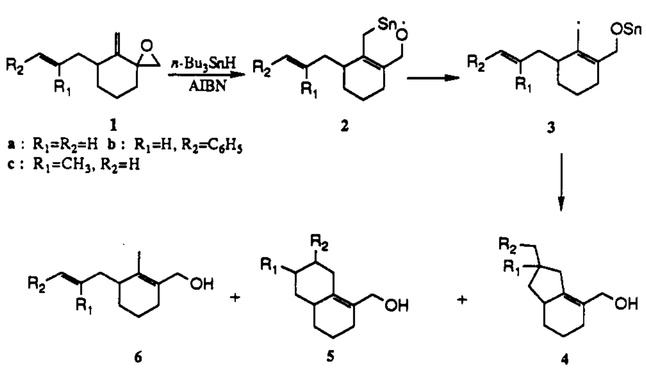
Radical reactions of vinyl epoxides have received little attention[1] despite their synthetic usefulness,[2] and we are unaware of any studies of *n*-Bu$_3$Sn radical addition to vinyl epoxides, which serves as a starting point for the generation of allylic or alkyl radicals via translocation of radical sites.[3] We wish to report novel sequential radical reactions of vinyl epoxides utilizing 1,5-*n*-Bu$_3$Sn group or 1,5-hydrogen atom transfer from carbon to oxygen, depending on the structural nature of vinyl epoxides.

Although very little is known on 1,5-transfers of heteroatoms bearing d orbitals[3] such as organosilicon[4] and organotin groups,[5] the ease of a 1,5-*n*-Bu$_3$Sn group transfer to an alkoxy radical is anticipated on the basis of three factors. First, the C–Sn bond is much weaker than the C–H bond and an alkoxy radical would abstract a 1,5-*n*-Bu$_3$Sn group rather than a hydrogen atom. Second, 1,5-*n*-Bu$_3$Sn abstraction should be facile because of the presence of the α-vinyl group. Third, a favorable geometry for 1,5-*n*-Bu$_3$Sn transfer is realized with **2**. The reaction of the vinyl exo epoxide **1** with *n*-Bu$_3$SnH occurred smoothly, yielding initially the alkoxy radical **2** bearing allyltin moiety. 1,5-*n*-Bu$_3$Sn transfer in **2** proceeded rapidly and cleanly, yielding the allylic radical **3** which underwent cyclization as shown in Scheme I.

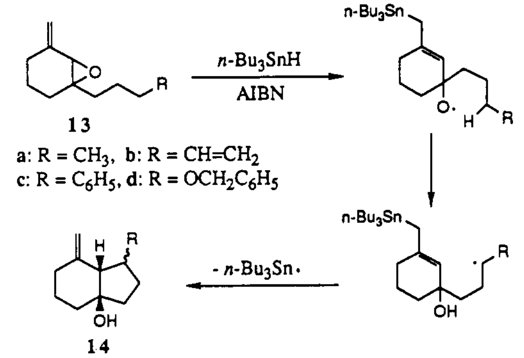
Scheme I[a]



a : $R_1=R_2=H$ b : $R_1=H, R_2=C_6H_5$
c : $R_1=CH_3, R_2=H$

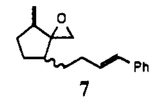
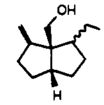
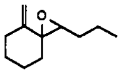
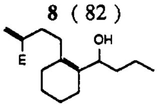
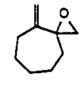
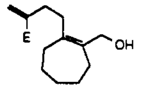
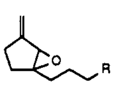
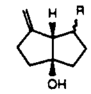
[a] Sn = *n*-Bu$_3$Sn.

Scheme II



a: R = CH$_3$, b: R = CH=CH$_2$
c: R = C$_6$H$_5$, d: R = OCH$_2$C$_6$H$_5$

Table I. Radical Reactions of Vinyl Epoxides[a]

vinyl epoxide	method	product (yield, %)[b]
1a	A	**4a** (12), **5a** (50), **6a** (24)
1b	A	**4b** (89)
1c	A	**5c** (84)
 **7**	A	 **8** (82)
 **9**	B[c] B[d]	 **10a** : E = COOEt (70) **10b** : = CN (86)
 **11**	B[c] B[d]	 **12a** : E = COOEt (63) **12b** : = CN (87)
13a : R = CH$_3$	C	**14a** (60)
13b : = CH=CH$_2$	C	**14b** (76)
13c : = C$_6$H$_5$	C	**14c** (82)
13d : = OCH$_2$C$_6$H$_5$	C	**14d** (73)
 **15a** : R = C$_6$H$_5$	C	 **16a** (60)
15b : = OCH$_2$C$_6$H$_5$	C	**16b** (58)

[a] The ratio of diastereomers is shown in ref 24. [b] The yield refers to the isolated yield and was not optimized. [c,d] Allylations were done with 2-carbethoxy- and 2-cyanoallyltri-*n*-butylstannane, respectively.

The radical reaction of a vinyl exo epoxide[6] was carried out by the addition of a 0.05 M benzene solution of *n*-Bu$_3$SnH (1.2 equiv) and AIBN (0.1 equiv) by a syringe pump for 3 h to a 0.025 M refluxing benzene solution of a vinyl epoxide and an additional stirring for 1 h (method A). As shown in Table I, cyclization reactions depend largely on the nature of substituents.[7,8] The

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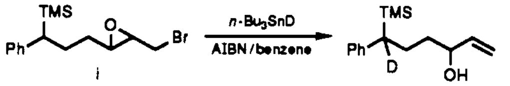
(1) Huyser, E. S.; Munson, L. R. *J. Org. Chem.* **1965**, *30*, 1436. Stogryn, E. L.; Gianni, M. H. *Tetrahedron Lett.* **1970**, *11*, 3025. Suzuki, A.; Miyaura, N.; Itoh, M.; Brown, H. C.; Holland, G. W.; Negishi, E.-i. *J. Am. Chem. Soc.* **1971**, *93*, 2792. Murphy, J. A.; Patterson, C. W.; Wooster, N. F. *Tetrahedron Lett.* **1988**, *29*, 955.

(2) For recent reports, see: Trost, B. M.; Sudhakar, A. R. *J. Am. Chem. Soc.* **1988**, *110*, 7933. Oshima, M.; Yamazaki, H.; Shimizu, I.; Nisar, M.; Tsuji, J. *J. Am. Chem. Soc.* **1989**, *111*, 6280 and references cited therein.

(3) Reviews: Beckwith, A. L. J.; Ingold, K. U. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4. Freidlina, R. Kh.; Terent'ev, A. B. *Adv. Free Radical Chem.* **1980**, *6*, 1.

(4) As far as we are aware, 1,5-TMS transfer has not been reported. According to our preliminary experiment (i → ii), 1,5-TMS transfer from benzylic carbon to oxygen did not occur, indicative of a strong preference for 1,5-H transfer over 1,5-TMS transfer, probably due to the stabilizing effect of the TMS group (Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1989**, *30*, 4413). A similar phenomenon has been recently observed by Curran (Snieckus, V.; Cuevas, J.-C.; Sloan, C. P.; Liu, H.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 896).



i

ii, 68%

(5) For one example of 1,5-*n*-Bu$_3$Sn transfer from enoxyl oxygen to alkoxy oxygen, see: Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1978**, *155*, 25.

(6) Vinyl exo epoxides (**1a**,**1b**,**1c**) were prepared from cyclohexanone in seven steps (LDA, allyl bromide/LDA, HCHO/MsCl–pyridine, DBU/NaBH$_4$–CeCl$_3$/*t*-BuOOH, VO(acac)$_2$/Swern/KOC(CH$_3$)$_3$, Ph$_3$PCH$_3$Br, toluene, reflux).

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vinyl epoxide **1b** with a cinnamyl substituent afforded exclusively the 5-exo product **4b** whereas **1a** afforded a mixture of **4a**, **5a**,[9] and **6a**[10] in a ratio of 12:50:24.[11] The exclusive 6-endo cyclization was realized with **1c** bearing β-methyl substituent[9] and **4c** was not detected. Although the present results are somewhat in contrast with previously reported strong preference for 5-exo cyclization of allylic radicals,[12] it is also well-known that cyclization of stabilized radicals is reversible, allowing thermodynamically favored 6-endo products to compete or even dominate.[13] Furthermore, the control of radical sites in cyclization by introducing a suitable substituent makes the present method versatile and attractive, as seen in **7**.[14]

The radical allylation of allylic halides and related precursors by allylstannanes has not been thoroughly studied.[15,16] Initial attempts with allyltri-*n*-butylstannane and methallyltri-*n*-butylstannane under the standard conditions (0.5 M toluene solution of allylstannane (2.0 equiv) and AIBN (0.1 equiv) at 80 °C for 2 h, method B) failed and starting vinyl epoxides were recovered unchanged. However, it has been found that allylation reactions proceeded smoothly with activated allylstannanes such as 2-carbethoxyallyltri-*n*-butylstannane[15b] and 2-cyanoallyltri-*n*-butylstannane.[17] Thus, treatment of **9** with activated allylstannanes afforded **10a** and **10b**.

The radical reaction of the vinyl endo epoxide **13** was similarly initiated by *n*-Bu_3Sn radical addition, followed by epoxide fragmentation to the alkoxy radical, 1,5-H transfer to produce the carbon centered radical, cyclization,[18] and termination via ejection of *n*-Bu_3Sn radical to afford the cis-fused bicyclic compound as shown in Scheme II.[19,20] The addition of a 0.05 M benzene solution of *n*-Bu_3SnH (0.3 equiv) and AIBN (0.05 equiv) by a syringe pump for 3 h to a 0.05 M refluxing benzene solution of **13a**[21] and an additional stirring for 1 h (method C) afforded **14a** in 60% yield as a 3:2 mixture of diastereomers. The use of the substrate bearing a radical stabilizing group on the side chain improved the yield.[22] The cyclopentenone-derived vinyl epoxide **15**[23] led to **16** in lower yield, as compared with **13**.

In conclusion, radical reactions of vinyl epoxides with *n*-Bu_3SnH proceed via radical translocations by a novel 1,5-*n*-Bu_3Sn group or a 1,5-hydrogen atom transfer, provide access to allylic or other carbon centered radicals for use in cyclization or addition reaction, and are highly useful for the synthesis of a variety of carbocyclic compounds.

Acknowledgment. We are indebted to the Organic Chemistry Research Center and Lucky Ltd. for financial support of this work. We thank Dr. Sung-Eun Yoo and Dr. Chwang Siek Pak of KRICT for their help in the structure determination.

Supplementary Material Available: Spectral data (^1H NMR, ^{13}C NMR, IR, and HRMS) for vinyl epoxides and products (7 pages). Ordering information is given on any current masthead page.

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(7) Recent reviews: Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. Curran, D. P. *Synthesis* **1988**, 417, 489.

(8) For cyclization of allyl radicals, see: Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 9272 and references cited therein.

(9) The structures of **5a** and **5c** were determined by unambiguous synthesis.

(10) For the sake of convenience, the regioisomeric product (the homoallylic alcohol from quenching the tertiary allylic radical by H) is not drawn in Scheme I and its benzoate was inseparable from the benzoate of **6a**. ^1H NMR analysis indicated the presence of a 3:1 mixture of **6a** and the regioisomer.

(11) A mixture of crude products was converted into the corresponding benzoates and the benzoates were separated with HPLC.

(12) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911.

(13) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. Laird, E. R.; Jorgensen, W. L. *J. Org. Chem.* **1990**, *55*, 9 and references cited therein.

(14) **7** was prepared from *N*-(cyclopentylidene)cyclohexylamine in four steps (LDA, $BrCH_2CH_2CH{=}CHPh$/LDA, HCHO/MsCl-pyridine, DBU/$Me_2S^+CH_2^-$.

(15) (a) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (b) Baldwin, J. E.; Adlington, R. M.; Birch, D. J.; Crawford, J. A.; Sweeney, J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1339. (c) Lee, E.; Yu, S.-G.; Hur, C.-U.; Yang, S.-M. *Tetrahedron Lett.* **1988**, *29*, 6969.

(16) Only one example of allylation of allyl bromide with allyltri-*n*-butylstannane under UV was reported (Grignon, J.; Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1975**, *96*, 225). However, reaction of 1-bromo-2-nonene with allyltri-*n*-butylstannane under standard Keck conditions did not occur.

(17) 2-Cyanoallyltri-*n*-butylstannane was prepared from 3-hydroxy-2-methylenepropanesulfonylbenzene (Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1987**, *28*, 6053) in four steps (Swern/NH_2OH-HCl-pyridine/$(CF_3CO)_2O$, Et_3N/*n*-Bu_3SnH, AIBN).

(18) It may be appropriate to mention that Rawal et al. reported the similar approach based on 1,5-H transfer and cyclization process during our investigation. Rawal, V. H.; Newton, R. C.; Krishnamurthy, V. *J. Org. Chem.* **1990**, *55*, 5181.

(19) Keck, G. E.; Enholm, E. J. *Tetrahedron Lett.* **1985**, *26*, 3311. Danishefsky, S. J.; Panek, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 917.

(20) The stereochemistry of the ring junction is expected to be cis due to geometrical and stereoelectronic reasons. Stork, G.; Mook, R.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741. Beckwith, A. L. J.; Roberts, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893 and ref 18.

(21) **13** was prepared from 2-cyclohexen-1-one in four steps (RLi/PCC/H_2O_2-NaOH/Wittig reaction).

(22) The only detectable byproduct was an enone (<5%), resulting from β-cleavage of the tertiary alkoxy radical.

(23) **15** was prepared from 2-bromo-2-cyclopenten-1-one in four steps (RMgBr, CuBr, Me_2S, TMSCl/LiCl, DMF/H_2O_2-NaOH/Wittig reaction).

(24) **1a**, 70:30; **1b**, 55:45; **1c**, 65:35; **4a**, 65:35; **4b**, 75:25; **5c**, 80:20; **7**, 75:25; **8**, 67:33; **14a**, 60:40; **14b**, 60:40; **14c**, 75:25; **14d**, 50:50; **16a**, 52:48; **16b**, 50:50. The ratio of **1a**, **1b**, **4a**, and **4b** was determined by HPLC and the ratio of the others was determined by ^1H NMR.

Symmetry Effects in Photoinduced Electron Transfer Reactions

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Electronic symmetry rules have been established for many types of chemical reactions.[1a] The existence of symmetry rules for electron-transfer reactions is of fundamental[1b,c] and practical interest, in view of efforts to develop strategies for the generation of long-lived charge-transfer states.[2] Experimental[3-6] and the-

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(1) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970. (b) Glauser, W. A.; Raber, D. J.; Stevens, B. *J. Phys. Chem.* **1991**, *95*, 1976. (c) Stevens, B. *Chem. Phys.* **1988**, *122*, 347.

(2) (a) Gust, D.; Moore, T. *Science* **1989**, *244*, 35. (b) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562.

(3) (a) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (c) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (d) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 8740. (e) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751. (f) Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 1319.

(4) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (b) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751. (c) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958. (d) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 5127. (e) Verhoeven, J. W. *Pure Appl. Chem.* **1990**, *62*, 1585. (f) Lawson, J. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1989**, *164*, 120. (g) Warman, J. M.; Smit, K. J.; de Haas, M. P.; Jonker, S. A.; Paddon-Row, M. N.; Oliver, A. M.; Kroon, J.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1991**, *95*, 1979. (h) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1988**, *150*, 366.

(5) (a) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635. (b) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1732. (c) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948. (d) Schanze, K. S.; Cabana, L. A. *J. Phys. Chem.* **1990**, *94*, 2740.

(6) (a) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596. (b) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571.

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