Homolytic 1,6-Transfer of the Bu3Sn Group from Allylic Carbon to Alkoxy Oxygen

Sunggak Kim* and Kwang Min Lim

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

A novel 1,6-Bu3Sn group transfer from allylic carbon to alkoxy oxygen is observed in radical reactions of vinyl oxetanes; it is greatly favoured over 1,5- and 1,6-hydrogen atom transfer.

1,5- and 1,6-hydrogen atom transfers are the most studied paths among radical rearrangements[1] and they have useful synthetic applications.[2] Radical rearrangement of Group 4 elements involving R_3Si, R_3Ge and R_3Sn group transfers has not been actively investigated,[3] although the reaction should be feasible because of the release in bond energy accompanying rearrangement. Davies and Tse have presented evidence for 1,5-Bu_3Sn group transfer from enoxy oxygen to alkoxy oxygen.[4] Recently, we have reported novel radical cyclizations utilizing 1,5-Bu_3Sn group transfers from allylic carbon to alkoxy oxygen[5] and from enoxy oxygen to alkoxy oxygen.[6] In connection with our continuing interest in radical rearrangements, we turned our attention to 1,6-Bu_3Sn group transfer reactions. The homolytic bond dissociation energy for the C–H bond is roughly 29 kcal mol^{-1} (1 cal = 4.184 J) greater than for the C–Sn bond and it is estimated that the 1,6-Bu_3Sn transfer in 2 would be thermodynamically favoured by ca. 39 kcal mol^{-1} whereas 1,5- and 1,6-hydrogen transfer would be favoured by ca. 19 kcal mol^{-1}.[7]

To explore the interesting possibilities of 1,6-Bu_3Sn transfer and competition between 1,5-hydrogen, 1,6-hydrogen and 1,6-Bu_3Sn transfer, the vinyl oxetanes 1 were prepared by routine operations. Reaction of 1 (n = 1 and 2) with Bu_3SnH in the presence of azoisobutyronitrile (AIBN) in refluxing benzene was not successful, yielding a recovery of ca. 50% of starting material even after 24 h. When the reaction was carried out in refluxing xylene using di-*tert*-butyl peroxide (DTBP) as an initiator, the reaction proceeded smoothly. As shown in Scheme 1, in order to differentiate between the products 5 and 6, resulting from 1,6-hydrogen transfer and direct quenching, the remaining reactions were carried out with Bu_3SnD. Reaction of 1 (0.05 mol dm^{-3} in xylene) with Bu_3SnD (1.2 equiv.) and DTBP (0.1 equiv.) in xylene at 140 °C for 16 h afforded an inseparable mixture of 3 and 4 as major products. Also produced in this reaction were 5, resulting from 1,6-hydrogen transfer of 2, and the direct quenching product 6. The ratio of 3a, 3b and 4 was determined by ^1H

NMR analysis in the olefinic region. Compound 4 was independently prepared in 48% yield by reaction of 1 (n = 1) with diphenyl disulfide (0.3 equiv.) and AIBN (0.1 equiv.) in refluxing benzene for 4 h and 3b was also prepared by
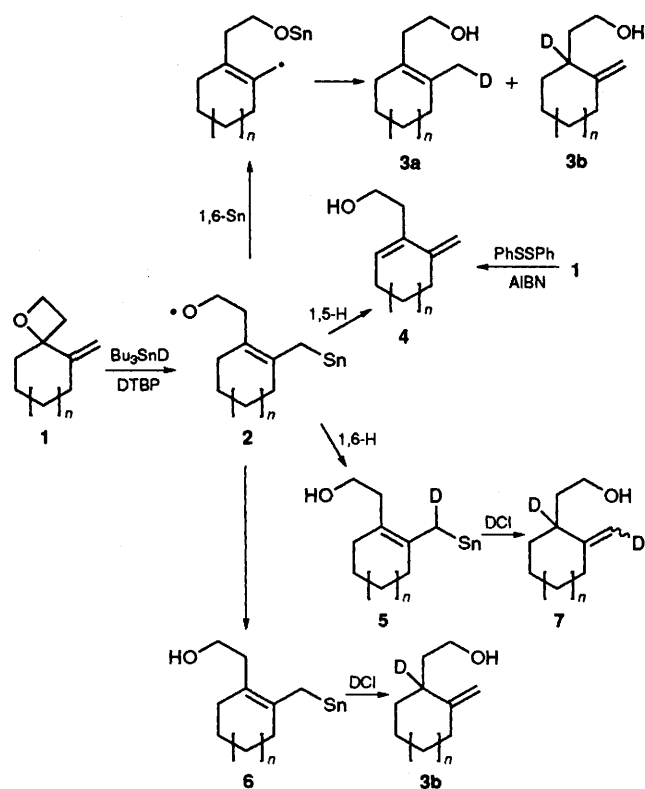
Scheme 1 Sn = Bu_3Sn

Table 1 Reactions of compounds **1** with tri-*n*-butyltin deuteride

Substrate	Yield (%)[a]	Product ratio			
		3a + 3b (3a/3b)[b]	4[b]	5[c]	6[c]
n =1	72	75 (88/12)	13	8	4
n =2	65	80 (75/25)	8	9	3
n =3	61	88 (92/8)	3	6	3

[a] Isolated yields. [b] The ratio was determined for a mixture of **3a**, **3b** and **4** by ¹H NMR. [c] The amount was determined by ¹H NMR, after destannylation of a mixture of **5** and **6**.

treatment of **6** with DCl. Furthermore, the ratio of **5** and **6** was similarly determined by ¹H NMR analysis of destannylated products (**3b**, **7**). Some experimental results are summarized in Table 1; several features are noteworthy. First, 1,6-Bu₃Sn transfer from carbon to oxygen is favoured over 1,6-hydrogen transfer by *ca.* 10 to 1. Secondly, 1,6-Bu₃Sn transfer is also greatly preferred over 1,5-hydrogen transfer. On the basis of the reported rate constant for 1,5-H transfer of *ca.* 10^8 s^{-1},[8] the rate constant for 1,6-Bu₃Sn transfer should be *ca.* 10^9 s^{-1}. Finally, the ratio of 1,5- to 1,6-hydrogen transfer in this study is *ca.* 1:1; the ratio of 1,5- to 1,6-hydrogen transfer from carbon to oxygen is *ca.* 10:1.[9] This striking result might be explained by stabilization due to the α-stannyl group or anchimeric assistance.[10]

References

1 A. L. J. Beckwith and K. U. Ingold, in *Rearrangement in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980; vol. I, p. 161; R. Kh. Freidlina and A. B. Terent'ev, *Adv. Free Radical Chem.*, 1980, **6**, 1.

2 For recent examples: A. D. Borthwick, S. Caddick and P. J. Parsons, *Tetrahedron Lett.*, 1990, **33**, 6911; V. H. Rawal, R. C. Newton and V. Krishnamurthy, *J. Org. Chem.*, 1990, **55**, 5181; D. P. Curran, K. V. Somayajula and H. Yu, *Tetrahedron Lett.*, 1992, **35**, 2295.

3 C. G. Pitt and M. S. Fowler, *J. Am. Chem. Soc.*, 1968, **90**, 1928; R. West and P. Boudjouk, *J. Am. Chem. Soc.*, 1973, **95**, 3983; A. Alberti and A. Hudson, *Chem. Phys. Lett.*, 1977, **48**, 331; Y.-M. Tsai and C. D. Cherng, *Tetrahedron Lett.*, 1991, **32**, 3515.

4 A. G. Davies and M.-W. Tse, *J. Organomet. Chem.*, 1978, **155**, 25.

5 S. Kim, S. Lee and J. S. Koh, *J. Am. Chem. Soc.*, 1991, **113**, 5106.

6 S. Kim and J. S. Koh, *J. Chem. Soc., Chem. Commun.*, 1992, 1378.

7 E. R. Laird and W. L. Jorgensen, *J. Org. Chem.*, 1990, **55**, 9.

8 B. C. Gilbert, R. G. G. Holmes, H. A. Laue and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1047.

9 J. Y. Nedelec and D. Lefort, *Tetrahedron*, 1975, **31**, 411; J. Y. Nedelec, M. Gruselle, A. Triki and D. Lefort, *Tetrahedron*, 1977, **33**, 39.

10 R. A. Jackson, K. U. Ingold, D. Griller and A. S. Nazran, *J. Am. Chem. Soc.*, 1985, **107**, 208 and references cited therein.