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SELECTIVE EPOXIDATION OF ALLYLIC ALCOHOLS WITH DIBUTYLTIN OXYPEROXIDE

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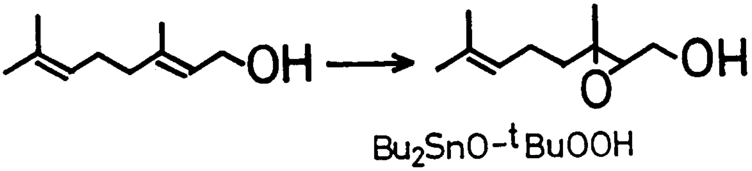
Abstract: Dibutyltin oxyperoxide derived from Bu_2SnO and ^tBuOOH epoxidize allylic alcohols with high stereo- and regioselectivities.

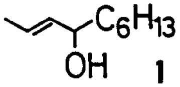
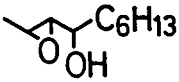
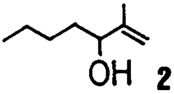
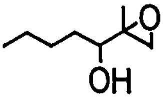
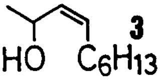
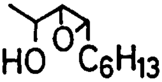
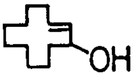
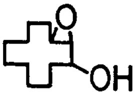
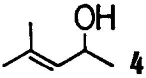
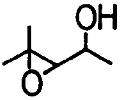
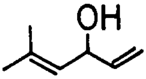
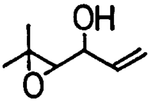
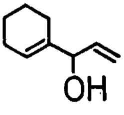
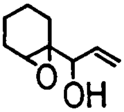
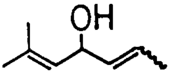
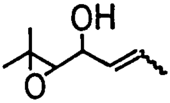
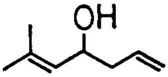
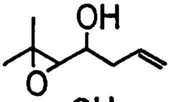
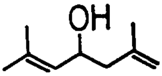
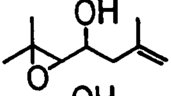
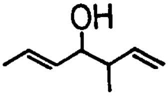
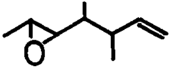
Epoxides are very useful as intermediates in organic synthesis.[1] Thus, extensive interest has been generated in the development of techniques to selectively epoxidize olefinic alcohols.[2] Many kinds of transition-metals are known to catalyze the epoxidation of olefins with hydroperoxides. Little is known, however, about efficient epoxidation by tin peroxy compounds. Here we wish to describe the selective epoxidation of allylic alcohols with dibutyltin oxyperoxide prepared from dibutyltin oxide and _t_-butylhydroperoxide.

A benzene solution of ^tBuOOH[3] (3.0 M, 1.0 ml, 3.0 mmol) was added to a suspension of Bu_2SnO[4] (0.25 g, 1.0 mmol) in benzene (8 ml). The mixture was heated at 60°C for 1 h to give a clear solution of dibutyltin oxyperoxide.[5] A solution of geraniol (0.16 g, 1.0 mmol) in benzene (2 ml) was added and the whole was heated at 60°C for additional 3 h. The resulting mixture was poured into aqueous NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with a saturated aqueous NaCl solution, and dried with Na_2SO_4. Evaporation of the solvent afforded a crude oil which was purified by preparative thin layer chromatography on silica gel to give 2,3-epoxygeraniol (0.14 g) in 83% yield. The isomer, 6,7-epoxygeraniol was not detected. Other data are summarized in Table 1.



The reaction rate heavily depends on the substitution pattern of the double bond. Thus, the reactivity of allylic alcohols toward dibutyltin oxyperoxide increases dramatically with increasing alkyl substitution. Mono-substituted allylic alcohol such as 1-dodecen-3-ol was recovered almost unchanged, whereas tetra-substituted olefin such as 2-cyclohexylidene-1-

Table 1. Epoxidation of Allylic Alcohols with Bu_2SnO-$^tBuOOH^a$

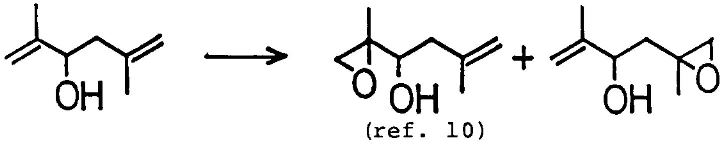
Entry	Alcohol	Reaction Time (h)	Product	Y(%)^b	T : E^{c,d}	VO(acac)$_2$ ^{t}BuOOH T : E^c
1	 **1**	6		75	40 : 60	20 : 80^e
2	 **2**	6		68	10 : 90	2 : 98^e
3	 **3**	6		83	95 : 5	71 : 29^e
4		6		90	27 : 73^f	29 : 71^e
5	 **4**	3		73	95 : 5	84 : 14
6		3		75^g	95 : 5	82 : 18
7		3		89	10 : 90	10 : 90
8		3		66	95 : 5	75 : 25
9		3		95	95 : 5	88 : 12
10		3		87	95 : 5	85 : 15
11		6		60	40 : 60	30 : 70

a) All reactions were performed at 60°C on one mmol scale. Bu_2SnO (1.0 mmol), ^tBuOOH (3.0 mmol), and alcohol (1.0 mmol) were employed. b) Isolated yields. c) The ratios were determined by glpc. See ref. 6. d) Threo and erythro. e) Cited from ref. 7. f) Trans : cis. g) See ref. 8.

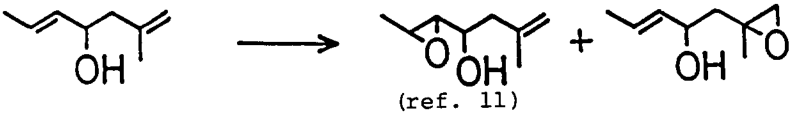
propanol was easily epoxidized to give the corresponding epoxy alcohol in 90% yield within one hour at 60°C. Alicyclic alcohols such as 2-cyclohexen-1-ol and 2-cycloocten-1-ol were reluctant to react and gave the corresponding epoxides in low yields (<5%) after prolonged heating at 60°C for 15 h.[9] One could hope for fairly selective epoxidation on a tri-substituted olefin in the presence of mono- or di-substituted one. This was indeed the case as demonstrated by the reactions described in Table 1 (Entry 6, 7, and 8).

The stereoselectivities obtained in the reaction with dibutyltin oxyperoxide are similar to those in the catalytic epoxidation with ^{t}BuOOH in the presence of $VO(acac)_2$.[7] Each system, however, has slightly different characteristics. The Bu_2SnO-^{t}BuOOH system provided high threo selectivity for the allylic alcohols, **3** and **4**. In contrast, $VO(acac)_2$-^{t}BuOOH gave erythro isomers for the alcohols, **1** and **2**, with high stereoselectivity. Toluene and chlorobenzene were equally effective as the solvent.

It is worth noting that the new system proved to be efficient for the selective epoxidation of the substrates which have two olfinic bonds such as 2,5-dimethyl-1,5-hexadien-3-ol and (E)-2-methyl-1,5-heptadien-4-ol. The Bu_2SnO-^{t}BuOOH system provided α,β-epoxyalcohols exclusively. Meanwhile previously reported three procedures gave mixtures of two isomers.[12,13]



Bu_2SnO-^{t}BuOOH	75%	100 (E/T = 95/5)	:	0
$VO(acac)_2$-^{t}BuOOH		87 (E/T = 98/2)	:	13
$Al(O^{t}Bu)_3$-^{t}BuOOH		67 (E/T = 85/15)	:	33
$Ti(O^{i}Pr)_4$-^{t}BuOOH		70 (E/T = 67/33)	:	30

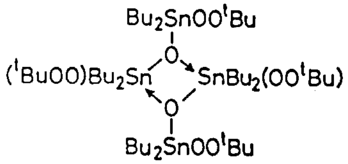


Bu_2SnO-^{t}BuOOH	70%	100 (E/T = 50/50)	:	0
$VO(acac)_2$-^{t}BuOOH		64 (E/T = 75/25)	:	36
$Al(O^{t}Bu)_3$-^{t}BuOOH		84 (E/T = 35/65)	:	16
$Ti(O^{i}Pr)_4$-^{t}BuOOH		70 (E/T = 40/60)	:	30

References and Notes

1. C. H. Behrens and K. B. Sharpless, Aldrichimica Acta, **16**, 67 (1983); S. Masamune and W. Choy, ibid., **15**, 47 (1982).

2. K. B. Sharpless, *Chemtech.*, **1985**, 692.
3. J. G. Hill, B. E. Rossiter, and K. B. Sharpless *J. Org. Chem.*, **48**, 3607 (1983).
4. Dioctyltin oxide was as effective as dibutyltin oxide. We thank Oogi Chemical Industry Co. Ltd. for the gift of these tin compounds.
5. A. G. Davies and I. F. Grahan, *Chem. Ind.*, **1963**, 1622. They isolated the peroxide depicted on the right side from Bu_2SnO and two equivalents of ^tBuOOH. We made the complex in situ and used directly for epoxidation without purification.



6. K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **21**, 1657 (1980); H. Tomioka, K. Takai, K. Oshima, and H. Nozaki, *ibid.*, **21**, 4843 (1980).
7. K. Itoh, K. Jitsukawa, K. Kaneda, S. Teranishi, *J. Amer. Chem. Soc.*, **101**, 159 (1979); E. D. Mihelich, *Tetrahedron Lett.*, **1979**, 4729; B. E. Rossiter, T. R. Verhoeven, K. B. Sharpless, *ibid.*, **1979**, 4733.
8. Bp. 75°C (bath temp, 15 Torr); IR (neat) 3412, 2962, 2928, 1426, 1380, 1118, 1030, 993, 925, 902, 820 cm^{-1}; NMR (200 MHz, $CDCl_3$) δ 1.35 (s, 6H), 2.78 (d, J = 7.6 Hz, 1H), 4.03 (m, 1H), 5.26 (d, J = 11 Hz, 1H), 5.38 (d, J = 18 Hz, 1H), 5.95 (ddd, J = 18, 11, 5.5 Hz, 1H). Found: C, 65.33; H, 9.50%. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44%.
9. 2-Cycloocten-1-ol was recovered almost quantitatively and 2-cyclohexen-1-ol was recovered in 60% yield along with 2-cyclohexen-1-one (10%).
10. Bp. 85°C (bath temp, 15 Torr); IR (neat) 3428, 3072, 2970, 2934, 1648, 1453, 1375, 1280, 1063, 1020, 895, 736, 698 cm^{-1}; NMR (200 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.80 (s, 3H), 2.10 (dd, J = 13, 8 Hz, 1H), 2.20-2.40 (m, 1H), 2.64 (d, J = 4.5 Hz, 1H), 2.90 (d. J = 4.5 Hz, 1H), 4.80-4.90 (m, 2H). Found: C, 67.32; H, 10.21%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92%.
11. Bp. 90°C (bath temp, 15 Torr); IR (neat) 3398, 2968, 2926, 1648, 1448, 1377, 1106, 1082, 1045, 1023, 875 cm^{-1}; NMR (200 MHz, $CDCl_3$) δ 1.33 (d, J = 5.5 Hz, 3H), 1.78 (s, 3H), 2.35 (m, 2H), 2.75 (m, 1H), 2.80-3.25 (m, 2H), 3.50-3.75 (m, 0.5H, threo isomer), 3.75-3.90 (m, 0.5H, erythro isomer), 4.83 (bs, 1H), 4.90 (bs, 1H). Found: C, 67.47; H, 10.00%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92%.
12. In these three reactions, ^tBuOOH (0.2 mmol) and substrate (1.0 mmol) were employed to prevent the formation of diepoxides. Thus, the yields of monoepoxides were not determined.
13. Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant in-aid for Scientific Research (C) # 60550608) is acknowledged.

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