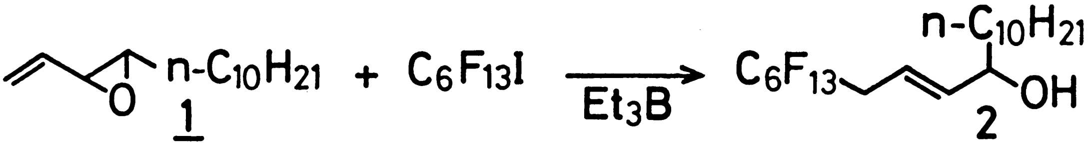
CHEMISTRY LETTERS, pp. 1437-1440, 1988. © 1988 The Chemical Society of Japan

Et_3B-Induced Radical Reaction of 1,3-Diene Monoxide with $C_6F_{13}I$, PhSH, or Ph_3GeH

Yoshifumi ICHINOSE, Koichiro OSHIMA,* and Kiitiro UTIMOTO
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606

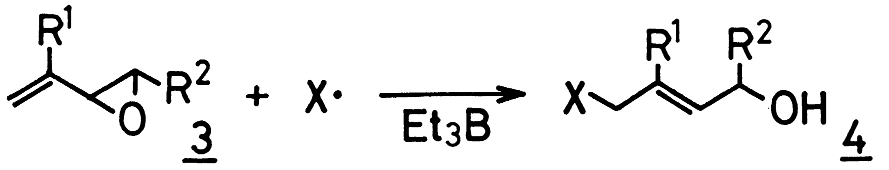
Treatment of 3,4-epoxy-1-butene with $C_6F_{13}I$, PhSH, or Ph_3GeH in the presence of Et_3B provides 4-substituted-2-buten-1-ol in good yield. Et_3B-Ph_3SnH mediated intramolecular alkylation of 1,3-diene monoxide are also described.

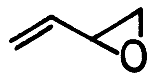
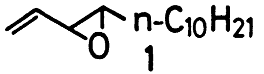
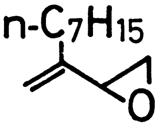
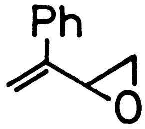
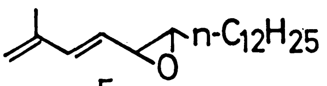
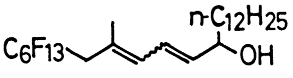
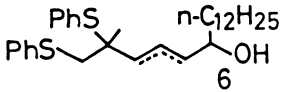
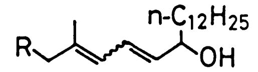
Recently we have reported that the 1,4-addition of alkyl radical generated from alkyl iodide to a double bond of α,β-unsaturated carbonyl compound in the presence of Et_3B gives boron enolate which reacts with an aldehyde to afford β-hydroxy carbonyl compound.[1] Further extension of this reaction to 1,3-diene monoxide as substrate has provided us with a novel synthetic route to 4-substituted-2-buten-1-ols.[2,3] A hexane solution of Et_3B[4] (1.0 M, 1 M = 1 mol dm^{-3}, 4.0 ml, 4.0 mmol) was added to a solution of 3,4-epoxy-1-tetradecene **1** (0.21 g, 1.0 mmol) and $C_6F_{13}I$ (1,78 g, 4.0 mmol) in benzene (5 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at 25 °C for 17 h. The mixture was poured into water and extracted with ethyl acetate (3x20 ml). The combined organic layers were dried (Na_2SO_4) and concentrated and the residual oil was submitted to silica gel column chromatography to give E-allylic alcohol **2** (0.52 g)[5] in 99% yield. The representative results are summarized in Table 1.



The yield of **2** decreased from 99% to 63% with decrease of molar amounts of $C_6F_{13}I$ and Et_3B employed from 4.0 mmol to 2.0 mmol each. However, use of a catalytic amount of Pd catalyst improved the yield significantly.[6] Thus, treatment of 1,3-butadiene monoxide (1.0 mmol) with $C_6F_{13}I$ (2.0 mmol) and Et_3B (2.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.05 mmol) at 25 °C for 17 h produced the desired allylic alcohol **2** in 78% yield. The palladium catalysis was not so effective for the reaction with other radical sources such as PhSH and Ph_3GeH. Acetonitrile was a solvent of choice for the reaction of 1,3-diene monoxide with Ph_3GeH. For instance, the reaction of 1,3-butadiene monoxide with Ph_3GeH in acetonitrile gave **4** ($R^1 = R^2 = H$, $X = Ph_3Ge$) in 85% yield. Meanwhile, only 37% yield was obtained in benzene. 1,3-Cycloocatadiene monoxide was recovered

Table 1. Et_3B-Induced radical reaction of 1,3-diene monoxide[a)]

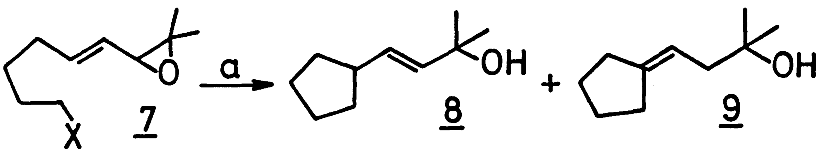


Entry	Substrate	Radical source	Solvent	Reaction time/h	Yield of 4/%
1		$C_6F_{13}I$	Benzene	11	66
2		PhSH	Benzene	10	73
3		Ph_3GeH	CH_3CN	10	85
4		Ph_3SnH	Benzene	10	31
5	 1	$C_6F_{13}I$	Benzene	17	99
6		CBr_4[b)]	Benzene	8	45
7		$BrCCl_3$	Benzene	14	45
8		PhSH	Benzene	11	47[c)]
9		Ph_3GeH	CH_3CN	11	55
10		$C_6F_{13}I$	Benzene	2	59 (57:43)[d)]
11		PhSH	Benzene	5	41 (50:50)[d,e)]
12		Ph_3GeH	CH_3CN	6	84 (71:29)[d)]
13		$C_6F_{13}I$	Benzene	0.5	77
14	 5	$C_6F_{13}I$	Benzene	0.5	 31
15		PhSH	Benzene	0.5	 6 69
16		Ph_3GeH	Benzene	2.0	 R=Ph_3Ge: 43 R=Et: 26

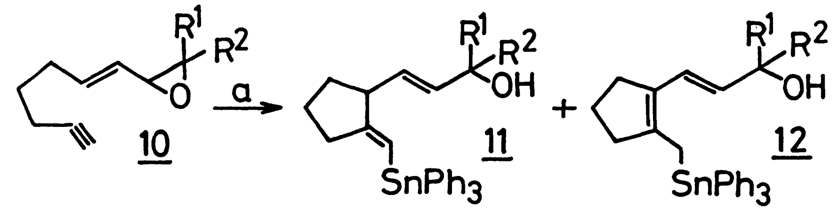
a) The reactions were performed at 25 °C. 1,3-Diene monoxide (1.0 mmol), radical source (4.0 mmol), and Et_3B (4.0 mmol) were employed unless otherwise noted. b) Monoxide (1.0 mmol), CBr_4 (1.2 mmol), and Et_3B (1.2 mmol) were employed. The use of large excess of CBr_4 gave a complex mixture. c) See Ref. 7. d) The structures (cis and trans) of the products could not be determined. e) Isomeric product, $PhSCH=C(n\text{-}C_7H_{15})CH_2CH_2OH$ was also obtained in 20% yield.

unchanged upon treatment with $C_6F_{13}I$ and Et_3B at 25 °C after prolonged reaction period (24 h).[8] The Et_3B-mediated reaction of triene monoxide **5** with PhSH gave a isomeric mixture of 1,2-bis(phenylthio)-6-hydroxy-2-methyloctadecene **6** derived from a facile addition of second molecule of thiol to monoadduct, $PhSCH_2C(CH_3)=CH-CH=CHCH(OH)-n-C_{12}H_{25}$.[9]

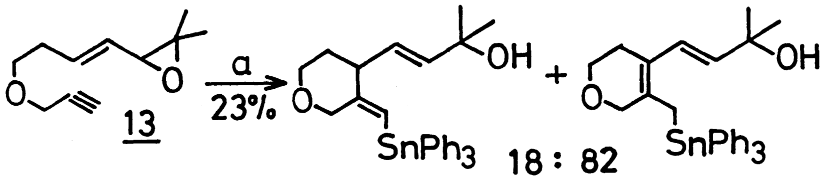
The reaction was applied to cyclization reaction shown below. A hexane solution of Et_3B (1.0 M, 2.0 ml, 2.0 mmol) was added to a solution of Ph_3SnH (0.70 g, 2.0 mmol) and diene monoxide **7** (or **10**, 1.0 mmol) in benzene (100 ml) at 25 °C under an argon atmosphere. After stirring for 15 h at 25 °C, the reaction mixture was poured into water and extracted with ethyl acetate. Purification by silica-gel column chromatography gave the cyclized product **8** and **9**[10,11] (or **11** and **12**) as a isomeric mixture in fair yield. Treatment of **13** with Et_3B-Ph_3SnH afforded the six-membered cyclized product in 23% yield along with the uncyclized alkenylstannane derived from hydrostannation of acetylenic bond (59%).[12,13]



X = Br 48% **8** : **9** = 64 : 36
X = I 48% **8** : **9** = 60 : 40



R^1 = $n-C_8H_{17}$ R^2 = H 52% **11** : **12** = 43 : 57
R^1 = R^2 = CH_3 62% 11 : 12 = 18 : 82



a: $Ph_3SnH-Et_3B$, benzene

References

1) K. Nozaki, K. Oshima, and K. Utimoto, Tetrahedron Lett., 29, 1543 (1988).

2) Oxygen-induced addition of R_3B to 1,3-butadiene monoxide has been reported. A. Suzuki, N. Miyaura, M. Itoh, H. C. Brown G. W. Holland, and E. Negishi, J. Am. Chem. Soc., 93, 2792 (1971).

3) The reaction of diene monoxide with R_2CuLi or (RCuCN)Li has been reported. R. J. Anderson, J. Am. Chem. Soc., 92, 4978 (1970); J. P. Marino and H. Abe, ibid., 103, 2907 (1981). Et_2AlSPh: A. Yasuda, M. Takahashi, and H. Takaya, Tetrahedron Lett., 22, 2413 (1981). Pd(0) ($RCOCH_2COR^1$): M. Suzuki, A.

Watanabe, and R. Noyori, J. Am. Chem. Soc., 101, 1623 (1979); B. M. Trost and G. A. Molander, ibid., 103, 5969 (1981); T. Takahashi, A. Ootaka, and J. Tsuji, Tetrahedron Lett., 25, 1921 (1984).

4) We thank Toyo Stauffer Chemical Company for a gift of Et_3B.

5) Examination of ^{1}H-NMR showed that the product **2** was a pure trans-isomer. δ 5.65 (dt, *J* = 16, 6.0 Hz, 1H) and 5.81 (dd, *J* = 16. 6.0 Hz, 1H).

6) Palladium catalysis in the addition of polyfluoromethane to olefins in the presence of Me_3Al has been reported. K. Maruoka, H. Sano, Y. Fukutani, and H. Yamamoto, Chem. Lett., 1985, 1689.

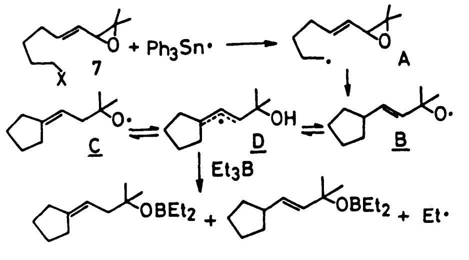
7) Mp 47-48 °C; IR (KBr) 3380, 2916, 2846, 1481, 1465, 1438, 1331, 1092, 958, 731, 687 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, *J* =6.5 Hz, 3H), 1.24 (bs, 19H), 3.53 (d, *J* = 6.6 Hz, 2H), 3.95-4.09 (m, 1H), 5.52 (dd, *J* = 6.6, 15.3 Hz, 1H), 5.70 (dt, *J* = 6.6, 15.3 Hz, 1H), 7.15-7.49 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ5.1, 14.1, 22.7, 25.2, 29.3, 29.5, 29.6, 31.9, 35.5, 36.0, 37.1, 72.4, 126.1, 126.4, 128.7, 130.3, 135.5, 136.5. Found: C, 74.61; H, 10.26%. Calcd for $C_{20}H_{32}OS$: C, 74.94; H, 10.06%.

8) Heating a benzene solution of 1,3-cyclooctadiene monoxide (1.0 mmol) and benzenethiol (1.2 mmol) at 80 °C in the presence of Et_3B (1.2 mmol) gave 4-hydroxy-3-phenylthio-1-cyclooctene in 69% yield.

9) Addition of thiol to conjugated systems are generally faster than addition to comparable isolated double bonds. K. Gnesbaum, Angew. Chem., Int. Ed. Engl., 9, 273 (1970).

10) ^{1}H-NMR ($CDCl_3$) of **8** and **9**: δ5.59-5.65 (m, **8**), 5.33-5.44 (tm, *J* = 7.5 Hz, **9**). Epoxidation of a mixture of **8** and **9** with mCPBA gave the corresponding epoxides **8'** and **9'** which were separated by preparative tlc. **8'**: δ2.70 (d, *J* = 2.5 Hz, 1H), 2.89 (dd, *J* = 2.5, 6.5 Hz, 1H); **9'**: δ3.24 (dd, *J* = 4.0, 8.0 Hz, 1H).

11) The formation of isomerized products **11** is presumably ascribed to the following mechanism: (1) the attack of triphenyltin radical on halide to give a radical **A**, (2) the radical **A** adds to olefinic bond intramolecularly to give an alkoxy radical **B**, (3) isomerization to a radical **C** through allylic radical **D**, and (4) finally react with Et_3B to give boron oxide and regenerate ethyl radical.



12) The addition of Ph_3GeH or CBr_4 to terminal olefins proved to proceed easily. For instance, treatment of 1-dodecene (1.0 mmol) with CBr_4 (4.0 mmol) or Ph_3GeH (4.0 mmol) in the presence of Et_3B (4.0 mmol) in benzene at 25 °C for 15 h provided 1,1,1,3-tetrabromododecane or 1-triphenylgermyldodecane in 85% or 96% yield, respectively. The reactions with internal olefins were sluggish and the corresponding adducts were obtained in low yields (~10%).

13) Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid for Special Project Research No. 62215017) is acknowledged.

(Received May 31, 1988)