## Regiospecific Conversion of Oxiranes into Primary Alcohols via Reaction with Organotin Derivatives

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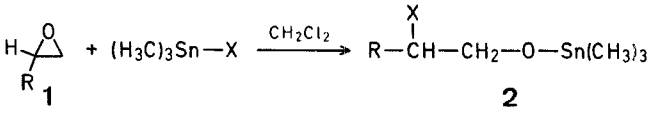
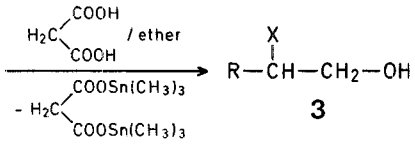
Oxiranes are versatile intermediates for the synthesis of several types of bifunctional compounds[1]. A variety of reagents may be used to cleave the oxirane ring; however, only in a few cases could a regiospecific cleavage be achieved[2,3].

The recent discovery that organosilicon compounds can be used for the conversion of oxiranes into allylic alcohols[4] caused us to investigate the reaction of Group IV B organometallics with these cyclic compounds[5]. We report here a new general method for opening the oxirane ring **(1)** using organotin derivatives. In this manner, 2-substituted alkanols **(3)** may be obtained in high yields via the stannyl ethers **2.**



**1** **2**



**3**

The reaction is regiospecific, probably due to the strong affinity of the Sn-atom to the O-atom of the oxirane ring which is independent of the types of organotin compound and oxirane used. Thus, organotin derivatives containing Sn—N, Sn—O, Sn—Cl, and Sn—J bonds insert rapidly into the ring of 2-methyloxirane, 2-phenyloxirane, and of 7-oxabicyclo[4.1.0]heptane; the intermediate stannoxanes **2** are obtained in high yields after 6–36 h at reflux from equimolar amounts of organometallic compound and oxirane in dichloromethane as solvent (Table 1). The stannoxy products **2** are quite stable and can be purified by vacuum distillation with the exception of **2h, i** which decompose spontaneously to the corresponding 2-alkylaminocyclohexanols **3h, i.** Destannylation of **2a–g** with malonic acid according to Ref.[6] affords the 2-amino-, 2-halo-, and 2-phenoxyalkanols **3** (Table 2). The homogeneity of these products was established by G.L.C., $^1$H-N.M.R., and $^{13}$C-N.M.R. analyses and their structures were supported by the I.R. absorption bands[7] in the region $\nu = 1040$–$1095$ cm$^{-1}$.

The above results contrast with the known behavior of oxiranes in ring-cleavage reactions; these reactions which occur upon treatment of an oxirane with an appropriate reagent, usually are not regiospecific and may therefore lead to sometimes only difficultly separable mixtures of primary and secondary bifunctional alcohols[8,9]. The few available data on the synthesis of isomerically pure aminoalkanols do not generally refer to cleavage reactions of oxiranes but to the reduction of aminoaldehydes or related compounds[9].

Our new route to functionally substituted alkanols of the type **3** has several advantages such as stability and ready availability of the reagents, lack of side reactions, high yields, and simple performance and thus provides a useful alternative to the hitherto known methods.

**2-Diethylaminopropoxytrimethylstannane (2a); Typical Procedure:**
A mixture of propylene oxide (methyloxirane; 0.5 g, 8.6 mmol), diethylaminotrimethylstannane (2 g, 8.6 mmol), and dichloromethane (5 ml) is refluxed under nitrogen for 16 h. The solvent is removed and the residual product purified by distillation in vacuo.

**2-Diethylaminopropanol (3a); Typical Procedure:**
A solution of 2-diethylaminopropoxytrimethylstannane (**2a**; 1 g, 3.4 mmol) in dry ether (5 ml) is added to a solution of malonic acid (0.17 g, 1.7 mmol) in dry ether (5 ml) and the mixture is refluxed for 2 h. After cooling, the mixture is filtered to remove bis[trimethylstannyl] malonate, the filtrate is evaporated, and the residue distilled to give **3a**; yield: 0.4 g (98%); b.p. 167 °C/760 torr.

**Table 1.** 2-Substituted Alkyl Trimethylstannyl Ethers (**2**)

| Oxirane **1** | X | Reaction time [h][a,b] | **2** | Yield[c] [%] | b.p. [°C]/ torr | $^1$H-N.M.R. ($CDCl_3$/$TMS_{int}$) $\delta$ [ppm] |
|---|---|---|---|---|---|---|
|  |  | 16 | **a** | 80 | 50°/3 | 0.35 (s, 9H); 1.12 (d, 3H); 1.21 (t, 6H); 3.27 (m, 6H); 3.71 (m, 1H) |
| |  | 16 | **b** | 70 | 50°/0.5 | 0.20 (s, 9H); 0.93 (d, 3H); 1.28 (m, 6H); 2.75–3.15 (broad m, 6H); 3.60 (m, 1H) |
| | $OC_6H_5$ | 8[d] | **c** | 80 | 134°/3 | 0.27 (s, 9H); 1.25 (d, 3H); 3.75 (d, 2H); 4.09 (m, 1H); 6.82 (m, 2H); 7.10 (m, 3H) |
| | Cl | 36 | **d** | 80 | 40°/30 | 0.35 (s, 9H); 1.12 (t, 3H); 3.27 (d, 2H); 3.71 (m, 1H) |
| | J | 1[e] | **e** | 80 | 54°/0.6 | 0.55 (s, 9H); 1.21 (d, 3H); 3.11 (d, 2H); 3.75 (m, 1H) |
|  |  | 8 | **f** | 80 | 93°/0.7 | 0.27 (s, 9H); 0.96 (t, 6H); 2.50 (q, 4H); 4.58 (t, 1H); 7.18 (m, 5H) |
| |  | 6 | **g** | 85 | 123°/0.5 | 0.19 (s, 9H); 1.32 (m, 6H); 2.23 (m, 4H); 3.61 (m, 2H); 4.51 (t, 1H); 7.01 (m, 5H) |
|  |  | 24 | **h** | —[f] | | |
| |  | 24 | **i** | —[f] | | |

[a] In boiling dichloromethane.
[b] Catalytic amounts of $ZnCl_2$ do not affect the reaction times.
[c] The microanalyses were in acceptable agreement with the calculated values: C, ±0.38; H, ±0.39; N, ±0.43.
[d] Without solvent at 80 °C.
[e] At room temperature.
[f] Products were not isolated.

**Table 2.** 2-Functionally Substituted Alkanols (**3**) by Destannylation of **2**

| **3** | Yield [%] | b.p. [°C]/torr | | I.R. (neat) $\nu_{C=O}$ [$cm^{-1}$] |
|---|---|---|---|---|
| | | found | reported | |
| **a** | 98 | 167°/760 | 166°/760[10] | 1064 |
| **b** | 99 | 58°/3.5 | 102°/20[11] | 1080 |
| **c** | 97 | 98°/5 | 120°/10[8] | 1045 |
| **d** | 98 | 124°/760 | 121°/760[12] | 1090 |
| **e** | 98 | 60°/10 | 74–79°/20[13] | 1065 |
| **f** | 97 | 111°/16 | 128°/21[14] | 1060 |
| **g** | 98 | 165°/0.1 | 102–104°/0.002[15] | 1065 |
| **h** | 45 | 101°/2.5 | 137°/20[16] | 1078 |
| **i** | 75 | 109°/5 | 230°/760[17] | 1082 |

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