

## Carbonyl Allylation by Vinyl Epoxides with $\text{SnCl}_2$ -TBA or $\text{SnCl}_2$ -LiI: Application to the Diastereoselective Synthesis of 1,3-Diols

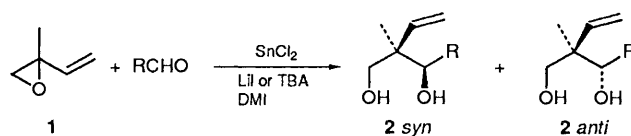
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Vinyl epoxides reacted with aldehydes in the presence of stannous chloride-tetrabutylammonium bromide or stannous chloride-lithium iodide to produce 2-vinyl-1,3-diols regio- and diastereoselectively.

Vinyl epoxides fail to undergo palladium-catalysed carbonyl allylation with  $\text{SnCl}_2$  via the formation of a  $\pi$ -allylpalladium complex,<sup>1</sup> in contrast to their allylation with allylic alcohol and ester.<sup>2</sup> Transformation of vinyl epoxides to 4-metaloxybut-2-enylmetal intermediates can, however, be promoted by LiI and applied to carbonyl allylation.<sup>3</sup> A reducing metal reagent such as anhydrous  $\text{CrCl}_2$  is unsuitable for carbonyl allylation since it is unstable in the presence of water and air. Here we report that tetrabutylammonium bromide (TBA) or LiI induces carbonyl allylation by vinyl epoxides with  $\text{SnCl}_2$  to produce 1,3-diols regio- and diastereo-selectively in the presence of water and air.

Some representative results of carbonyl allylation by 3,4-epoxy-3-methylbut-1-ene **1** with  $\text{SnCl}_2$  in 1,3-dimethylimidazolidin-2-one (DMI) are summarized in Table 1 (Scheme 1). The addition of LiI led to the same regio- and diastereo-



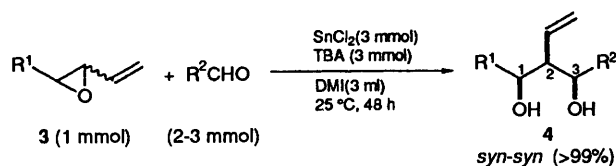
Scheme 1

selectivity as those in the carbonyl allylation by **1** with  $\text{CrCl}_2$ -LiI. Water contained in hydrated LiI did not suppress the carbonyl allylation. TBA, which was not a Lewis acid, was also effective for the *syn*-selective carbonyl allylation. The carbonyl allylation did not occur in the absence of  $\text{LiI}\cdot 2\text{H}_2\text{O}$  and TBA even at 50 °C. Use of THF as a solvent depressed the yield (66%) and the *syn* selectivity (*syn/anti* = 50:50) in the carbonyl

**Table 1** Carbonyl allylation by **1** with SnCl<sub>2</sub>-LiI or SnCl<sub>2</sub>-TBA<sup>a</sup>

Aldehyde	Additive	Temp(°C)	Time(h)	<b>2</b> , Yield(%)	<i>syn:anti</i> <sup>b</sup>
<i>p</i> -MeOCC <sub>6</sub> H <sub>4</sub> CHO	LiI·2H <sub>2</sub> O	50	5	88	84:16
<i>p</i> -MeOCC <sub>6</sub> H <sub>4</sub> CHO	LiI·2H <sub>2</sub> O	25	6	96	92:8
<i>p</i> -MeOCC <sub>6</sub> H <sub>4</sub> CHO	TBA	50	5	83	83:17
<i>p</i> -MeOCC <sub>6</sub> H <sub>4</sub> CHO	TBA	25	7	90	92:8
PhCHO	TBA	25	16	89	93:7
3,4-(CH <sub>2</sub> O <sub>2</sub> )C <sub>6</sub> H <sub>3</sub> CHO	TBA	25	16	89	93:7
( <i>E</i> )-PhCH=CHCHO	TBA	25	19	45	83:17
C <sub>6</sub> H <sub>13</sub> CHO	TBA	25	24	35	71:29
<i>c</i> -C <sub>6</sub> H <sub>11</sub> CHO	TBA	25	15	37	94:4

<sup>a</sup> The addition of 3,4-epoxy-3-methylbut-1-ene **1** (3 mmol) to aldehydes (1 mmol) with SnCl<sub>2</sub> (3 mmol) and additive (LiI·2H<sub>2</sub>O or TBA; 3 mmol) was carried out in DMI (3 ml). <sup>b</sup> See ref. 2: the diastereoisomer ratio was determined by comparison of <sup>1</sup>H NMR spectra with authentic samples presented by Dr. K. Takai and Prof. K. Utimoto

**Scheme 2**

allylation of *p*-methoxycarbonylbenzaldehyde by **1** at 25 °C for 20 h.

Carbonyl allylation by 4-substituted 3,4-epoxybut-1-enes **3**\* instead of **1** was carried out with SnCl<sub>2</sub>-TBA in DMI to give only 1,2-*syn*-2,3-*syn*-2-vinyl-1,3-diols **4**† [R<sup>1</sup> = Ph, R<sup>2</sup> = *p*-MeO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>, 48%; R<sup>1</sup> = Ph, R<sup>2</sup> = 3,4-(CH<sub>2</sub>O<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>, 28%; R<sup>1</sup> = Ph, R<sup>2</sup> = C<sub>6</sub>H<sub>13</sub>, 28%; R<sup>1</sup> = C<sub>6</sub>H<sub>13</sub>, R<sup>2</sup> = *p*-MeO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>, 32%; R<sup>1</sup> = C<sub>6</sub>H<sub>11</sub>, R<sup>2</sup> = *p*-MeO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>, 53%]. No by-products were detected in these reactions (see Scheme 2).<sup>5</sup> LiI·2H<sub>2</sub>O was also efficient for the carbonyl allylation by **3** (R<sup>1</sup> = Ph); the addition to *p*-methoxycarbonylbenzaldehyde with SnCl<sub>2</sub>-LiI·2H<sub>2</sub>O in DMI at 25 °C produced **4** (>99% *syn-syn*) in 48% yield. Diastereocontrol at three-carbon centres was achieved by the carbonyl allylation for a *cis-trans* mixture of **3** with SnCl<sub>2</sub>, unlike the case of CrCl<sub>2</sub> with which no reaction of 4-substituted 3,4-epoxybut-1-enes has been reported. 3-Substituted or 4-substituted 3,4-epoxybut-1-enes can function as synthons of 1-(1-hydroxyalkyl)prop-2-enyl carbanions, if SnCl<sub>2</sub>-TBA or SnCl<sub>2</sub>-LiI·2H<sub>2</sub>O is used.

## Experimental

**Carbonyl Allylation by 3,4-Epoxy-3-methylbut-1-ene 1 with SnCl<sub>2</sub>-TBA.**—To a solution of stannous chloride (0.57 g, 3 mmol) and TBA (0.97 g, 3 mmol) in DMI (3 ml) were added 3,4-epoxy-3-methylbut-1-ene **1** (0.25 g, 3 mmol) and 4-methoxycarbonylbenzaldehyde (0.16 g, 1 mmol). The mixture was stirred for 7 h at 25 °C after which it was diluted with water (20 ml) and extracted with methylene dichloride (100 ml). The extract was washed with water and brine, dried (MgSO<sub>4</sub>) and evaporated.

\* 4,4-Substituted 3,4-epoxybut-1-enes **3** were prepared from allyldimethylsulphonium bromide and aldehydes with sodium hydroxide in aqueous isopropylalcohol (R<sup>1</sup> = Ph, *cis/trans* = 40:60; R<sup>1</sup> = C<sub>6</sub>H<sub>13</sub>, *cis/trans* = 50:50; R<sup>1</sup> = *c*-C<sub>6</sub>H<sub>11</sub>, *cis/trans* = 44:56)

† The configuration of 1,3-diols **4** was determined by the conversion of **4** into 1,3-dioxane derivatives, followed by <sup>1</sup>H NMR spectroscopic investigation of the 1,3-dioxanes [<sup>1</sup>H NMR (CDCl<sub>3</sub>) J<sub>H<sup>1</sup>H<sup>2</sup></sub>: 1.9–2.3, J<sub>H<sup>2</sup>H<sup>3</sup></sub>: 1.9–2.3]

Column chromatography of the residue on silica gel (hexane-ethyl acetate, 1:2) afforded 1-(4-methoxycarbonylphenyl)-2-methyl-2-vinylpropane-1,3-diol **2** (R = *p*-MeO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>) (0.22 g, 90%; *syn:anti* = 92:8) as a colourless oil (R<sub>F</sub> 0.38, hexane-ethyl acetate, 1:2, on silica gel). The structure and the diastereoisomer ratio were determined by comparison of the <sup>1</sup>H NMR spectrum with an authentic sample;<sup>3</sup> ν<sub>max</sub>/cm<sup>-1</sup> 3420 (OH), 3070 (=CH<sub>2</sub>), 3020 (=CH), 3000 (H-Ph), 2950–2900 (CH<sub>3</sub>, CH<sub>2</sub>), 1730 (CO), 1620 (C=C), 1280, 1120 (COO) and 820 (Ph); δ<sub>H</sub>(270 MHz; solvent CDCl<sub>3</sub>; standard Me<sub>4</sub>Si) 0.86 (3 H, s, CH<sub>3</sub>), 3.47 (1 H, d, J 10.6, 3-H), 3.62 (1 H, d, J 10.6, 3-H), 3.75 (1 H, br, OH), 3.87 (3 H, s, CO<sub>2</sub>CH<sub>3</sub>), 4.30 (1 H br, OH), 4.70 (*syn*), 4.77 (*anti*) (1 H, s, 1-H), 4.91 (*syn*), 4.92 (*anti*) [1 H, dd, J 17.6 and 1.1, (*Z*)-HC=], 5.08 (*anti*), 5.14 (*syn*) [1 H, dd, J 11.0 and 1.1, (*E*)-HC=], 5.79 (*anti*), 6.00 (*syn*) (1 H, dd, J 17.6 and 11.0, CH=), 7.31 (2 H, d, J 8.4, 2- and 6-Ph) and 7.90 (2 H, d, J 8.4, 3- and 5-Ph).

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## References

- For formation of π-allylpalladium complexes from vinyl epoxides, see: J. Tsuji, H. Kataoka and Y. Kobayashi, *Tetrahedron Lett.*, 1981, **22**, 2575; B. M. Trost and G. A. Molander, *J. Am. Chem. Soc.*, 1981, **103**, 5969; A. M. Echavarren, D. R. Tueting and J. K. Stille, *J. Am. Chem. Soc.*, 1988, **110**, 4039; B. M. Trost and A. R. Sudhakar, *J. Am. Chem. Soc.*, 1988, **110**, 7933, and references cited therein.
- Y. Masuyama, R. Hayashi, K. Otake and Y. Kurusu, *J. Chem. Soc., Chem. Commun.*, 1988, 44; Y. Masuyama, K. Otake and Y. Kurusu, *Tetrahedron Lett.*, 1988, **29**, 3563; Y. Masuyama, J. P. Takahara and Y. Kurusu, *J. Am. Chem. Soc.*, 1988, **110**, 4473; Y. Masuyama, J. P. Takahara and Y. Kurusu, *Tetrahedron Lett.*, 1989, **30**, 3437; Y. Masuyama, T. Tsunoda and Y. Kurusu, *Chem. Lett.*, 1989, 1647; Y. Masuyama, Y. Nimura and Y. Kurusu, *Tetrahedron Lett.*, 1991, **32**, 225.
- O. Fujimura, K. Takai and K. Utimoto, *J. Org. Chem.*, 1990, **55**, 1705.
- M. J. Hatch, *J. Org. Chem.*, 1969, **34**, 2133.
- K. Koga and S. Yamada, *Chem. Pharm. Bull.*, 1972, **20**, 526.

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