

## Stereospecific Conversion of Iodohydrin Derivatives into Alkenes by Means of an Allylsilane-Titanium Tetrachloride System and its Application to Stereoretentive Deoxygenation of Epoxides

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**Abstract.** Whereas *erythro*-iodohydrin derivatives provided (*E*)-alkenes with high stereoselectivity upon treatment with titanium tetrachloride in the presence of allyltrimethylsilane, the corresponding *threo* isomers afforded (*Z*)-alkenes exclusively. The reaction was applied to the stereoretentive conversion of epoxides to alkenes. © 1997 Elsevier Science Ltd.

We have reported that the reaction of vicinal alkoxyiodoalkanes with butyllithium proceeds in *syn* fashion to give alkenes stereospecifically and that the interconversion of olefinic geometrical isomers has been performed by an *anti*-addition of an iodide-alkoxy moiety to an alkene and subsequent *syn* elimination of those groups.<sup>1</sup> Here we wish to report that the reaction of iodohydrin derivatives and their analogues with a TiCl<sub>4</sub>-allyltrimethylsilane system takes place in *anti*-fashion to provide olefins stereospecifically and that stereoretentive deoxygenation of epoxides has been achieved by successive treatment with tetrabutylammonium iodide and allyltrimethylsilane in the presence of titanium tetrachloride.

We examined a β elimination reaction of the vicinal acetoxyiodoalkanes<sup>2</sup> **1a** and **1b** with several Lewis acids such as TiCl<sub>4</sub>, SnCl<sub>4</sub>, BF<sub>3</sub>•OEt<sub>2</sub>, and TMSOTf (Scheme 1). Among them, titanium tetrachloride gave the best results in terms of yields and stereospecificity. Whereas *erythro*-acetoxyiodoalkane **1a** provided (*E*)-6-dodecene with high stereoselectivity, *threo*-isomer **1b** gave (*Z*)-6-dodecene almost exclusively (Table 1, entry 1 and 2). Tin(IV) chloride afforded the corresponding alkenes with high stereospecificity but in moderate or low yields. For instance, **1a** or **1b** provided (*E*)-6-dodecene (*E/Z* = >99/1) or (*Z*)-6-dodecene (*E/Z* = 8/92) in 38% or 52% yield, respectively, upon treatment with tin(IV) chloride in the presence of allyltrimethylsilane. Boron trifluoride, diethylaluminium chloride, and trimethylsilyl triflate were not effective for the conversion of **1a** and **1b** into olefins and the starting **1a** and **1b** were recovered unchanged.

### Scheme 1

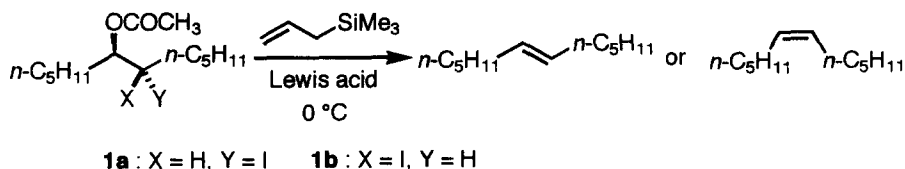
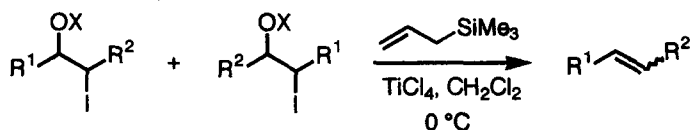


Table 1. Conversion of Iodohydrin Derivatives<sup>a</sup> into Alkenes

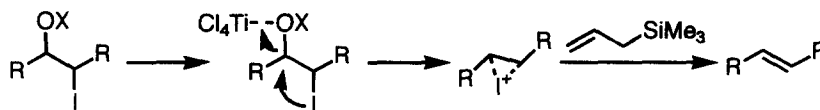
Entry	X	R <sup>1</sup>	R <sup>2</sup>	<i>erythro/threo</i>	Yield(%)	<i>E/Z</i>	
1	<b>1a</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	>99/1	91	97/3
2	<b>1b</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<1/99	97	4/96
3	<b>1c</b>	CH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	>99/1	93	98/2
4	<b>1d</b>	CH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	4/96	85	4/96
5	<b>1e</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	>99/1	85	98/2
6	<b>1f</b>	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	3/97	84	8/92
7	<b>1g</b>	SiMe <sub>2</sub> - <i>t</i> -Bu	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	>99/1	22	>99/1
8	<b>1h</b>	SiMe <sub>2</sub> - <i>t</i> -Bu	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<1/99	26	4/96
9	<b>1i</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	CH <sub>3</sub>	>99/1	77	>99/1
10	<b>1j</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	>99/1	81	>99/1
11	<b>1k</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	5/95	84	5/95
12	<b>1l</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	>99/1	48	85/15
13	<b>1m</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	6/94	69	11/89
14	<b>1n</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	97/3	88	97/3
15	<b>1o</b>	COCH <sub>3</sub>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	6/94	76	12/88

a) Starting materials **1c** and **1d** were prepared by iodoetherization from *E*-6-dodecene and *Z*-6-dodecene. Acetates (**1a** and **1b**) and silyl ethers (**1g** and **1h**) were prepared from iodohydrins (**1e** and **1f**). Acetates **1i–1p** were generated from the corresponding iodohydrins.

Next, the conversion of several iodohydrin derivatives<sup>3</sup> into alkenes was studied using a titanium tetrachloride-allyltrimethylsilane combination. The representative results are also shown in Table 1. Several comments are worth noting: (1) Elimination proceeded in *anti*-fashion. (2) Iodohydrin itself and methyl ether as well as vicinal acetoxyiodoalkane were converted into olefins with high stereospecificity in good yields. On the other hand, *t*-butyldimethylsilyl ethers gave the corresponding alkenes in only 22–26% yields and starting materials were recovered in 60–70% yield. (3) A regioisomeric mixture of unsymmetrical iodohydrin derivatives also afforded the corresponding alkenes in good yields. (4) The acetoxyiodoalkanes (**1j–1o**) having other functional groups in the molecule could be converted into the corresponding alkenes stereospecifically. However, the selectivities were slightly inferior to those for **1a–1h**.<sup>4</sup>

We are tempted to assume the following reaction mechanism. The coordination of oxygen of the methoxy or acetoxy group to titanium tetrachloride would facilitate the elimination of those groups to give a bridged iodonium ion intermediate. An attack of allyltrimethylsilane on the iodonium ion would provide alkenes and allyl iodide.<sup>5</sup> The formation of allyl iodide was confirmed by the <sup>1</sup>H NMR examination of the reaction mixture (Scheme 2).

**Scheme 2**



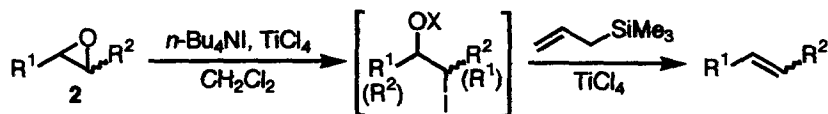
Then, the elimination reaction was applied to the stereospecific conversion of epoxides into alkenes. The deoxygenation of epoxides to olefins has been widely studied and numerous reagents have been reported to give the olefins nonstereospecifically through a radical intermediate.<sup>6</sup> Here we wish to describe that the successive treatment of epoxides with tetrabutylammonium iodide and allyltrimethylsilane in the presence of titanium tetrachloride provides olefins of the same geometry as epoxides.<sup>7,8</sup>

Deoxygenation was studied using *cis*- and *trans*-6-dodecene oxide as substrates. Treatment of epoxides with titanium tetrachloride and allyltrimethylsilane resulted in recovery of the starting epoxides. The use of titanium tetraiodide instead of titanium tetrachloride facilitated the ring opening of epoxides, but the yields of alkenes were disappointingly low (~40%) in spite of high stereospecificity after successive treatment with allyltrimethylsilane. Finally, we found that an addition of tetrabutylammonium iodide in the presence of titanium tetrachloride followed by treatment with allyltrimethylsilane provided alkenes with high stereospecificity in good yields. For instance, treatment of epoxide **2a** (*cis/trans* = <1/99) with tetrabutylammonium iodide, titanium tetrachloride, and allyltrimethylsilane at 0 °C gave (*E*)-6-dodecene (*Z/E* = <1/99) in 78% yield. Meantime, the stereoisomer **2b** (*cis/trans* = 92/8) afforded *Z*-6-dodecene with high selectivity (*Z/E* = 89/11). The overall retention of configuration can be explained by (1) S<sub>N</sub>2 opening of epoxide by iodide and (2) *anti*-elimination of the iodohydrin derivative.

Typical procedure for the deoxygenation of epoxides is as follows. A solution of titanium tetrachloride in dichloromethane (1.0 M, 3.0 ml, 3.0 mmol) was added to a solution of tetrabutylammonium iodide (0.40 g, 1.1 mmol) and epoxide **2a** (184 mg, 1.0 mmol) in dichloromethane (10 ml) at 0 °C under argon atmosphere. After the mixture was stirred for 15 min at 0 °C, allyltrimethylsilane (0.49 g, 4.0 mmol) was added. The resulting mixture was stirred for 2 h at 0 °C and poured into aqueous ammonium chloride solution. Extraction with hexane (20 ml X 3) followed by silica gel column purification afforded (*E*)-6-dodecene (0.12 g) in 78% yield.

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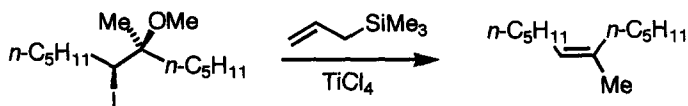
Table 2. One pot conversion of epoxides into alkenes



Entry	R <sup>1</sup>	Epoxide R <sup>2</sup>	cis/trans	Yield(%)	Z/E
1	<b>2a</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	<1/99	78	<1/99
2	<b>2b</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	92/8	62	89/11
3	<b>2c</b>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCOCH <sub>3</sub>	87/13	63	85/15
4	<b>2d</b>	(CH <sub>2</sub> ) <sub>8</sub> OH	93/7	83	92/8
5	<b>2e</b>	H	—	36	—

## References and Notes

- Maeda, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1996**, *61*, 6770–6771.
- The starting acetoxyiodoalkanes were prepared from the corresponding iodohydrins. Very recently samarium-mediated stereoselective synthesis of iodohydrins from 1,1-diodoalkanes and aldehydes has been reported. Matsubara, S.; Yoshioka, M.; Utimoto, K. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 617–618.
- Bromo- and chlorohydrin derivatives did not react under the same reaction conditions. The use of tosylate (*n*-C<sub>5</sub>H<sub>11</sub>CH(OMe)CH(OTs)*n*-C<sub>5</sub>H<sub>11</sub>) and mesylate (*n*-C<sub>5</sub>H<sub>11</sub>CH(OMe)CH(OMs)*n*-C<sub>5</sub>H<sub>11</sub>) resulted in formation of complex mixture.
- Treatment of **3** with titanium tetrachloride-allyltrimethylsilane provided tri-substituted alkene in 78% yield.



**3** : erythro/threo = 7/93

E/Z = 22/78

- An alternative mechanism is as follows. An attack of allyltrimethylsilane on the iodide of the substrate activated by TiCl<sub>4</sub> would provide alkenes *via anti*-periplanar elimination.
- (1) Kochi, J. K.; Singleton, D. M.; Andrews, L. J. *Tetrahedron*, **1968**, *24*, 3503–3515. (2) Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538–6540. (3) McMurry, J. E.; Silverstri, M. G.; Fleming, M. P.; Hoz, T.; Grayston, M. W. *J. Org. Chem.* **1978**, *43*, 3249–3255. (4) Sato, M.; Oshima, K. *Chem. Lett.* **1982**, 157–160. (5) Fujisawa, T.; Sugimoto, K.; Ohta, H. *Chem. Lett.* **1974**, 883–886.
- Other retentive deoxygenation of epoxide has been reported. Sonnet, P. E. *J. Org. Chem.* **1978**, *43*, 1841–1842; idem. *Synthesis* **1980**, 828–830; Caputo, R.; Mangoni, L.; Neri, O.; Palumbo, G. *Tetrahedron Lett.* **1981**, *22*, 3551–3552; Matsubara, S.; Nonaka, T.; Okuda, Y.; Kanemoto, S.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1480–1483.
- In contrast, the reaction with Me<sub>3</sub>SiK or PhMe<sub>2</sub>SiLi proceeded stereospecifically to give an olefin of geometry opposite to that of the starting epoxide. (1) Dervan, P. B.; Shippey, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 1265–1267. (2) Reetz, M. T.; Plachky, M. *Synthesis*, **1976**, 199–200.

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