

# Efficient and Catalytic Conversion of Epoxides to 1,3-Dioxolanes with $\text{TiO}(\text{TFA})_2$ or $\text{TiCl}_3(\text{OTf})^\dagger$

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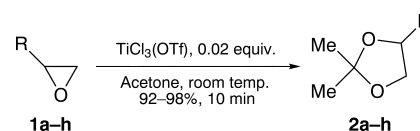
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$\text{TiO}(\text{TFA})_2$  or  $\text{TiCl}_3(\text{OTf})$  catalyses the efficient reaction of epoxides with acetone to give the corresponding 1,3-dioxolanes in excellent yields. The reaction of chiral styrene oxide was found to be highly stereospecific.

Direct conversion of an epoxide into a 1,3-dioxolane with acetone instead of adding water to form a diol with subsequent elimination is a subject of interest due to the importance of 1,3-dioxolanes as widely used protecting groups for diols<sup>1,2</sup> and particularly for carbohydrates and steroid chemistry. In addition, they are very suitable derivatives of diols for GC, GLC and mass spectrometry.<sup>3</sup> This transformation has been studied only with a few reagents. Among these, anhydrous copper sulfate<sup>3</sup> has been reported to produce the dioxolanes, but the yields in most cases are low with relatively long reaction times. The use of zeolite,<sup>4a</sup> KSF clay,<sup>4b</sup>  $\text{HBF}_4$ <sup>4c</sup> and some Lewis acids has been studied for this transformation. Most of the Lewis acids failed to give the desired product. Anhydrous zinc<sup>5</sup> and magnesium halides<sup>5,6</sup> have been reported to give rearranged products. The same reaction with both  $\text{FeCl}_3$ <sup>7</sup> or  $\text{Me}_3\text{SiCl}$ <sup>8</sup> gave the corresponding halohydrins, and  $\text{SnCl}_4$  and  $\text{TiCl}_4$  produced little or no product.<sup>9a</sup> However, the use of  $\text{TiCl}_4$  for conversion of only aryl-substituted epoxides into their corresponding acetals in moderate yield has been reported.<sup>9b</sup>

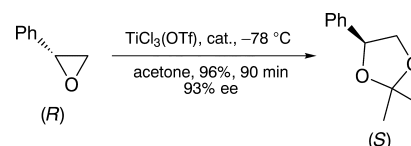
Among Lewis acids,  $\text{BF}_3 \cdot \text{OEt}_2$  has been successfully used for conversion of different types of carbonyl compounds into their corresponding 1,3-dioxolane derivatives with only ethylene and propylene oxides.<sup>9a</sup> There was no reaction of epoxides carrying electron-releasing groups. Although  $\text{TiCl}_4$  also gave no reaction, we observed that  $\text{TiO}(\text{TFA})_2$ <sup>10</sup> and  $\text{TiCl}_3(\text{OTf})$ <sup>11</sup> can catalyse the efficient reaction of epoxides with acetone to give 1,3-dioxolanes in excellent yields. These two known solid titanium(IV) compounds are stable and can be prepared from  $\text{TiCl}_4$ . Epoxides with both electron-releasing and withdrawing groups were treated with these catalysts in acetone. It was observed that  $\text{TiCl}_3(\text{OTf})$  is more efficient than  $\text{TiO}(\text{TFA})_2$ . Its reactions with epoxides and acetone occur at room temperature and only 0.02 molar equivalent of the catalyst is enough to convert epoxides into their corresponding 1,3-dioxolanes within 10 min in 92–98% yields (Scheme 1).



**Scheme 1** R or epoxide: **a** Ph, **b**  $n\text{-C}_4\text{H}_9$ , **c**  $\text{CH}_2=\text{CHCH}_2\text{OCH}_2$ , **d**  $\text{PhOCH}_2$ , **e**  $\text{ClCH}_2\text{OCH}_2$ , **f**  $(\text{CH}_3)_2\text{CHOCH}_2$ , **g** cyclohexene oxide, **h** cyclopentene oxide

The results obtained are shown in Table 1.

The reaction of *R*(+)-styrene oxide in the presence of 0.02 mol equiv. of  $\text{TiCl}_3(\text{OTf})$  was found to be highly stereospecific with inversion of configuration<sup>9b</sup> (Scheme 2).



**Scheme 2**

In conclusion this catalytic method can be applied for conversion of different classes of epoxides into their corresponding 1,3-dioxolanes. Excellent yields and stereo-specificity, short times, simple work-up and mild reaction conditions make this a useful procedure for this transformation.

## Experimental

Products were characterised by comparison of their physical data, IR, NMR and mass spectra with those of authentic samples. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer, NMR spectra on a Bruker Avance DPX-250 and mass spectra on a Shimadzu GCMS-QP 1000 EX. The purity determination of the substrates and reaction monitoring were by TLC on polygram SILG/UV 254 silica gel plates or GLC on a Shimadzu GC-10A instrument.

**Table 1** Conversion of epoxides into 1,3-dioxolanes catalysed with  $\text{TiO}(\text{TFA})_2$  or  $\text{TiCl}_3(\text{OTf})$  in acetone

Epoxide	Reaction with $\text{TiCl}_3(\text{OTf})$ at r.t.		Reaction with $\text{TiO}(\text{TFA})_2$ under reflux	
	Product <sup>a</sup> /yield (%) <sup>b</sup>	Molar equiv. of cat./time (min)	Product/yield (%)	Molar equiv. of cat./time (h)
<b>1a</b>	<b>2a</b> /98	0.02/10	<b>2a</b> /90	0.06/0.6
<b>1b</b>	<b>2b</b> /93	0.02/10	<b>2b</b> /80	0.2/2
<b>1c</b>	<b>2c</b> /96	0.02/10	<b>2c</b> /90	0.15/1.3
<b>1d</b>	<b>2d</b> /97	0.02/10	<b>2d</b> /91	0.3/5
<b>1e</b>	<b>2e</b> /92	0.02/10	<b>2e</b> /78	0.2/1.4
<b>1f</b>	<b>2f</b> /95	0.02/10	<b>2f</b> /89	0.3/6
<b>1g<sup>c</sup></b>	<b>2g</b> /95	0.02/10	<b>2g</b> /85	0.1/0.6
<b>1h</b>	<b>2h</b> /93	0.02/10	<b>2h</b> /83	0.15/0.7

<sup>a</sup>Products were identified by comparison with known samples. <sup>b</sup>Isolated yield. <sup>c</sup>The stereochemistry of the product was found to be *trans*; confirmed by hydrolysis of the product and isolation of the corresponding *trans*-1,2 diol according to the literature.<sup>12</sup>

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*Reaction of Styrene Oxide with Acetone in the presence of  $\text{TiO}(\text{TFA})_2$ , Typical Procedure.*—Styrene oxide (0.121 g, 1 mmol) and  $\text{TiO}(\text{TFA})_2$  (0.06 mmol, 17.3 mg) were refluxed in dry acetone (3 ml) for 36 min. The reaction mixture was cooled to room

temperature, water (5 ml) added and stirred for 10 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15$  ml) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and after chromatography on a short column of silica gel with  $\text{CCl}_4$  or light petroleum the pure product was obtained as a colourless liquid (0.16 g, 90%).

*Reaction of Styrene Oxide with Acetone in the Presence of  $\text{TiCl}_3(\text{OTf})$ , Typical Procedure.*—Styrene oxide (0.121 g, 1 mmol) and  $\text{TiCl}_3(\text{OTf})$  (0.02 mmol, 6 mg) were stirred in dry acetone (3 ml) at room temperature for 10 min. Then 3 or 4 drops of tetra-*n*-butylammonium hydroxide and water (5 ml) were added and stirred for 10 min. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15$  ml) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and chromatography on a short column of silica gel with  $\text{CCl}_4$  or light petroleum gave the pure product as a colourless liquid (0.174 g, 98%).

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## References

- 1 T. H. Green and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd edn., Wiley, New York, 1991, pp. 188–195.
- 2 F. A. J. Meskens, *Synthesis*, 1981, 501.
- 3 R. P. Hanzlik and M. Leinwetter, *J. Org. Chem.*, 1978, **43**, 438.
- 4 (a) L. W. Zatorski and P. T. Wierzchowski, *Catal. Lett.*, 1991, **10**, 211; (b) H. Steinbrink, Chemische Werke Huls AG, *Ger. Pat. (DOS)*, 1086241, 1959 (*Chem. Abstr.*, 1962, **56**, 5969); (c) A. A. Gevorkyan, P. I. Kazaryan, O. V. Avakyan and R. A. Vardanyan, *Khim. Geterotsikl. Soedin*, 1991, **1**, 33 (*Chem. Abstr.*, 1991, **115**, 8633x).
- 5 B. Rickborn and R. M. Gerkin, *J. Am. Chem. Soc.*, 1971, **93**, 1693.
- 6 P. F. Hudrlik, R. N. Misra, G. P. Withers, H. M. Hudrlik, R. J. Rona and J. P. Arcoleo, *Tetrahedron Lett.*, 1976, 1453.
- 7 J. Kagan, B. E. Firth, N. Y. Shih and C. Boyajian, *J. Org. Chem.*, 1977, **42**, 343.
- 8 D. J. Harvey, *Res. Commun. Chem. Pathol. Pharmacol.*, 1972, **4**, 247.
- 9 (a) D. S. Torok, J. J. Figueroa and W. J. Scott, *J. Org. Chem.*, 1993, **58**, 7274; (b) T. Nagata, T. Takai, T. Yamada, K. Imagawa and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2614.
- 10 P. Sartori, *Angew Chem.*, 1964, **76**, 376.
- 11 (a) R. Nofle and G. H. Cady, *Inorg. Chem.*, 1966, **5**, 2182; (b) H. Moulay el Mustapha and J. L. Pascal, *J. Fluorine Chem.*, 1991, **55**, 63.
- 12 A. L. Shabanov, M. M. Movsumzade, N. G. Kerimova, A. S. Kyazimov and V. S. Mamedzade, *Uch. Zap. Azerb. Inst. Nefti Khim., Ser. 9*, 1971, **8**, 78.