This article was downloaded by: [North Carolina State University] On: 12 October 2012, At: 14:34 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

Bismuth(III) Chloride (BiCl₃); An Efficient Catalyst for Mild, Regio- and Stereoselective Cleavage of Epoxides with Alcohols, Acetic Acid and Water

I. Mohammadpoor-Baltork a , S. Tangestaninejad a , H. Aliyan a & V. Mirkhani a

^a Department of Chemistry, Esfahan University, Esfahan, 81744, Iran

Version of record first published: 04 Dec 2007.

To cite this article: I. Mohammadpoor-Baltork, S. Tangestaninejad, H. Aliyan & V. Mirkhani (2000): Bismuth(III) Chloride (BiCl₃); An Efficient Catalyst for Mild, Regioand Stereoselective Cleavage of Epoxides with Alcohols, Acetic Acid and Water, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:13, 2365-2374

To link to this article: <u>http://dx.doi.org/10.1080/00397910008086878</u>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

BISMUTH(III) CHLORIDE (BiCl₃); AN EFFICIENT CATALYST FOR MILD, REGIO- AND STEREOSELECTIVE CLEAVAGE OF EPOXIDES WITH ALCOHOLS, ACETIC ACID AND WATER

I. Mohammadpoor-Baltork*, S. Tangestaninejad, H. Aliyan and V. Mirkhani

Department of Chemistry, Esfahan University, Esfahan 81744, Iran

ABSTRACT: Epoxides can be cleaved in a regio- and stereoselective manner with alcohols, acetic acid and water in the presence of catalytic amounts of bismuth(III) chloride, affording the corresponding β -alkoxy and β -acetoxy alcohols and diols in high yields.

Epoxides are valuable intermediates in organic synthesis, and the strain of the ring makes them prone to react with a large number of organic compounds. Nucleophilic ring-opening of epoxides in the presence of an acid and a base has been extensively studied^{1.4}. Under the reported conditions, these reactions have limited applicability in modern organic synthesis. In most of the epoxide ringopening reactions under acidic conditions, the formation of a mixture of

^{*}To whom correspondence should be addressed.

regioisomers and polymerization is observed. Heterogeneous catalysts, such as Nafion-H⁵, dehydrated alumina⁶ and organotin phosphate codensates⁷ have achieved limited success in ring-opening reactions of epoxides; they suffer from disadvantages such as high acidity, the non-catalytic nature of the reagent, long reaction times and inconvenient handling; their application was confined to the involvement of only primary alcohols. Therefore, the introduction of new methods for the nucleophilic ring-opening of epoxides, which work under mild conditions, is still in demand and is important in synthetic organic chemistry. A number of methods using Lewis acids and one-electron transfer catalysts have also been reported for ring-opening reactions of epoxides with different nucleophiles⁸⁻²⁴.

Recently, we have reported the use of bismuth(III) chloride as catalyst for the conversion of oxiranes to thiiranes and deprotection of 1,1-diacetates^{25,26}. In this paper we now introduce bismuth(III) chloride as an efficient and convenient catalyst for the ring-opening reactions of various epoxides with different nucleophiles such as alcohols, acetic acid and water.

Results and Discussion

The alcoholysis of various epoxides such as cyclohexene and styrene oxides, (chloromethyl)oxirane, allyl oxiranylmethyl ether, isopropyl oxiranylmethyl ether and 1,2-epoxyoctane as examples of aliphatic, alicyclic, activated and deactivated epoxides, were performed with primary, secondary and tertiary alcohols, affording the corresponding β -alkoxy alcohols in high yields (Table 1). The reactions in the case of cyclohexene oxide were stereoselective,

and only the trans products were obtained (entries 1-5). In the case of unsymmetrical epoxides, the reactions are regioselective with an attack of the nucleophile (alcohol) on the less-substituted oxirane carbon to yield anti-Markovnikov type products (entries 6-25). The only exception is given by styrene oxide, in which the reactions occur on the more substituted carbon; Markovnikov type products were obtained (entries 26-30).

The reactions of these epoxides with acetic acid in the presence of catalytic amounts of bismuth(III) chloride occurred in the same manner as alcohols; high yields of the corresponding β -acetoxy alcohols were obtained (Table 2).

Hydrolysis of the epoxides was also performed in the presence of this catalyst in aqueous acetonitrile; the corresponding diols were obtained in high yields (Table 2).

In comparison with the reported results for some other reagents, such as $FeCl_3^{18}$, $FeCl_3/SiO_2^{21}$, ceric ammonium nitrate $(CAN)^{14,16}$, and lanthanide triflates^{12,24} the use of bismuth(III) chloride is more suitable. The use of anhydrous $FeCl_3$ suffers from the highly hygroscopic nature of the reagent. $FeCl_3/SiO_2$ has the disadvantages of bulk use of the reagent, and requries an excess of the solvent. In the case of CAN, in many reactions large amounts of the catalyst (up to 0.8 molar ratio) have been used to complete the reaction. It is worth mentioning that lanthanide triflates are very expensive reagents. Therefore, BiCl_3 as a nonhygroscopic and available reagent could be a good alternative for this transformation.

Run	Epoxide	R-OH/ Condition	BiCl ₃ /Epoxide Product ^a /Yield (%) ^b	
			(T, min.)	
			, · · ·	OR
1		R= CH ₃ /rt	0.1(30)	97
2		$R = C_2 H_5/rt$	0.1(120)	98
3		R= <i>n</i> -Pr/reflux	0.1(20)	99
4		R= <i>i</i> -Pr/reflux	0.1(25)	95
5		R= t-Bu/reflux	0.1(30)	93
	CICH2-CH-CH2			Cl-CH ₂ -CH-CH ₂ I I OH OR
6	0	R=CH ₂ /reflux	0.15(60)	87
7		$R = C_2 H_c/reflux$	0.2(60)	85
, 8		R = n - Pr/reflux	0.2(90)	80
9		R = i - Pr/reflux	0.25(120)	82
10		R = t-Bu/reflux	0.25(120)	80
	(CH3) 2CHOCH2 - CH-CH2			
	o			(CH ₃) ₂ CHO-CH ₂ -CH-CH ₂ OH OR
11		R= CH ₃ /reflux	0.1(75)	96
12		$R = C_2 H_5 / reflux$	0.1(120)	87
13		R= <i>n</i> -Pr/reflux	0.1(120)	85
14		R= <i>i</i> -Pr/reflux	0.15(90)	80
15		R= t-Bu/reflux	0.2(90)	80
	$\sim\sim\sim$ j			
		·		ОН
16		R= CH ₃ /reflux	0.05(35)	96

Table 1. Alcoholysis of Epoxides Catalyzed by BiCl₃

2368



a) The products were characterized by comparison with known samples.

b) Yields refer to isolated products.

In conclusion, we have introduced a new and efficient catalytic method for the alcoholysis, acetolysis and hydrolysis of epoxides. In addition, the advantages such as high regio- and stereoselectivity, ease of handling, availability, stability and non-toxicity of the catalyst, high yields and short reaction times, make this

Run	Époxide	Solvent/ Condition	BiCl ₃ /Epoxide (T, min.)	Product ^a /Yield (%) ^b
1	CH-CH2	H2O/CH3CN/ rt	0.1(30)	СП-СН-СН2 ОН ОН 96
2	CH-CH-CH2	CH3CO2H/ rt	0.2(30)	CH-CH ₂ I I OACOH 87
3	\bigcirc°	H2O/CH3CN/ rt	0.15(45)	он
4	○	CH3CO2H/ rt	0.15(120)	OH OAc 80
5	ClcH ₂ -CH-CH ₂	H ₂ O/CH ₃ CN/ reflux	0.2(120)	C1CH ₂ -CH-CH ₂ I I OH OH 86
6	C1CH ₂ -CH-CH ₂	CH3CO2H/ reflux	0.15(120)	ClCH ₂ -CH-CH ₂ I I OH OAC 79
7	(CH ₃) ₂ CHOCH ₂ -CH-CH ₂	H ₂ O/CH ₃ CN/ reflux	0.2(40)	(СН ₃) ₂ СНОСН ₂ -СН-СН ₂ 1 ОН ОН 75
8	(CH ₃) ₂ CHOCH ₂ -CH-CH ₂	CH₃CO₂H/ reflux	0.2(30)	(CH ₃) ₂ CHOCH ₂ -CH-CH ₂ I I OH OAC
9	~~~~ů	H ₂ O/CH ₃ CN/ reflux	0.2(20)	91

Table 2. Hydrolysis and Acetolysis of Epoxides Catalyzed by BiCl3



a) The products were characterized by comparison with known samples.b) Yields refer to isolated products.

method a useful and important addition to the present methodologies in organic synthesis.

Experimental

Products were characterized by comparison of their physical data, IR and NMR spectra with those prepared in accordance with literature procedures^{14-16,18,21,24}. All yields refer to isolated products. IR spectra were run on a Philips PU9716 spectrophotometer. NMR spectra were recorded in CDCl₃ solvent on a Bruker AM 80 MHz spectrometer using TMS as an internal standard. GC analysis was performed with a Shimadzu 16A gas chromatograph with a flame ionization detector using a column of 15% Carbowax 20M Chromosorb-W 60-80 mesh.

Alcoholysis of Epoxides; General Procedure

Bismuth(III) chloride (0.25-1.25 mmol) was added to a solution of epoxide (5 mmol) in the appropriate alcohol (25 mL) and the mixture was stirred at room

temperature or under reflux conditions for 15-120 min. The progress of the reaction was monitored by GC. The solvent was evaporated. Water (15 mL) was added and the mixture was extracted with Et_2O (3x15 mL). The organic solution was dried (MgSO₄). Evaporation of the solvent followed by vacuum distillation or column chromatography on a short column of silica-gel afforded pure product; yields 78-99% (Table 1).

Acetolysis of Epoxides; General Procedure

A solution of epoxide (5 mmol) in acetic acid (25 mL) was treated with $BiCl_3$ (0.75-1 mmol) and the mixture was stirred at room temperature or under reflux conditions for 30-120 min. The progress of the reaction was monitored by GC. The solvent was evaporated. Water (15 mL) was added and the mixture was extracted with Et_2O (3x15 mL). The etherate was washed with a 5% solution of sodium hydrogencarbonate and dried. Evaporation of the solvent followed by vacuum distillation or column chromatography on a short column of silica-gel afforded pure product; yields 79-96% (Table 2).

Hydrolysis of Epoxides; General Procedure

To a solution of epoxide (5 mmol) in an equal mixture of CH_3CN , H_2O (25 mL) was added BiCl₃ (0.5-1 mmol) and the mixture was stirred at room temperature or under reflux conditions for 20-120 min. The reaction was monitored by GC. The reaction mixture was evaporated. The obtained aqueous mixture was saturated with brine and extracted with Et₂O (3x15 mL). The combined organic solution was dried and evaporated. Vacuum distillation or

column chromatography of the product on a short column of silica-gel afforded pure product; yields 75-98% (Table 2).

Acknowledgement : We are thankful to the Esfahan University Research Council for partial support of this work.

References:

- 1. Creteche, L. H. and Pittenger, W. H. J. Am. Chem. Soc. 1924, 46, 1503.
- Ashburn, H. V., Collect, A. R. and Lazzell, C. L. J. Am. Chem. Soc. 1935, 57, 1862.
- 3. Reeve, W. and Christoffer, I. J. J. Am. Chem. Soc. 1950, 72, 1480.
- 4. Winstein, S. and Henderson, R. B. J. Am. Chem. Soc. 1943, 65, 2196.
- 5. Olah, G. A., Fung, A. P. and Meider, D. Synthesis 1981, 280.
- Posner, G. H., Rogers, D. Z., Kinzig, C. H. and Gurria, G. M. Tetrahedron Lett. 1975, 16, 3597.
- Otera, J., Yoshinaya, Y. and Hirakawa, K. Tetrahedron Lett. 1985, 26, 3219.
- 8. Posner, G. H. and Rogers, D. Z. J. Am. Chem. Soc. 1977, 99, 8208.
- 9. Posner, G. H. and Rogers, D. Z. J. Am. Chem. Soc. 1977, 99, 8214.
- 10. Smith, J. G. Synthesis 1984, 629.
- 11. Bonini, C. and Righi, G. Synthesis 1994, 225.
- Chini, M., Crotti, P., Favero, L., Macchia, F. and Pineschi, M. Tetrahedron Lett. 1994, 35, 433.
- Iqbal, J., Khan, M. A. and Srivastava, R. R. Tetrahedron Lett. 1988, 29, 4985.

- Iranpoor, N. and Mohammadpoor-Baltork, I. Synth. Commun. 1990, 20, 2789.
- Iranpoor, N. and Mohammadpoor-Baltork, I. *Tetrahedron Lett.* 1990, 31, 735.
- Iranpoor, N., Mohammadpoor-Baltork, I. and Shiriny Zardaloo, F. Tetrahedron, 1991, 47, 9861.
- 17. Cheudary, B. M. and Sudha, Y. Synth. Commun. 1996, 26, 2989.
- 18. Iranpoor, N. and Salehi, P. Synthesis 1994, 1152.
- 19. Masaki, Y., Miura, T. and Ochiai, M. Synlett 1993, 847.
- 20. Masaki, Y., Miura, T. and Ochiai, M. Bull. Chem. Soc. Jpn. 1996, 69, 195.
- 21. Iranpoor, N., Tarrian, T. and Movahedi, Z. Synthesis 1996, 1473.
- Jacobsen, E. N., Kakiuchi, F., Konsler, R. G., Larrow, J. F. and Tokunaga, M. Tetrahedron Lett. 1997, 38, 773.
- Taniguchi, Y., Tanaka, S., Kitamura, T. and Fujiwara, Y. *Tetrahedron Lett.* 1998, 39, 4559.
- 24. Iranpoor, N., Shekarriz M. and Shiriny, F. Synth. Commun. 1998, 28, 347.
- Mohammadpoor-Baltork, I. and Aliyan H. Synth. Commun. 1998, 28, 3943.
- Mohammadpoor-Baltork, I. and Aliyan H. Synth. Commun. 1999, 29, 2741.

Received in Japan 7/21/99