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Samarium iodides catalyzed *meso*-epoxides ring opening by aromatic amines

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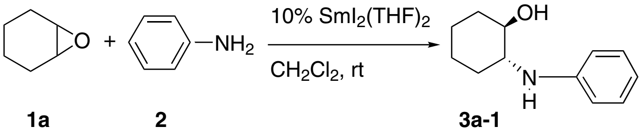
Abstract—Samarium diiodide catalyzes the ring opening of *meso*-epoxides by several aromatic amines affording β-aminoalcohols at room temperature. The use of bis-binaphthoxy iodo samarium allows an enantioselective desymmetrization of cyclohexene oxide by *o*-anisidine.

1. Introduction

The β-aminoalcohols are important organic compounds with numerous applications in medicinal and organic chemistry and as chiral auxiliaries for asymmetric synthesis.[1,2] They are typically obtained by ring opening of epoxides by amines but the use of elevated temperatures and excess of amines are often required to perform these reactions.[3] Since milder conditions are highly desirable to prepare sensitive molecules, various alternative methods have been studied, such as a variety of catalysts,[4–7] or reaction media such as fluorous solvents[8] and ionic liquids.[9] Amongst the different types of Lewis acids that have been described, metal halides,[5] triflates,[6] or lithium bistriflimide[7] are revealed as efficient catalysts for the ring opening of epoxides with aromatic amines.

The applications of lanthanide derivatives in catalysis have grown rapidly due to their high Lewis acid properties and their non-toxicity.[10] Lanthanide chlorides[5g,h] and triflates[6a,b] can thus be used for the ring opening reactions of epoxides. We have shown the interest of samarium diiodide as a Lewis acid type catalyst for various reactions, such as Mukaiyama aldol and Michael reaction, [4 + 2] cycloaddition and sequences of successive reactions including Mukaiyama Michael-aldol and Michael-iminoaldol tandem reactions.[11] In the course of these investigations we found that samarium diiodide and trivalent samarium iodides catalyze the ring opening of epoxides by amines and by silylated nucleophiles.[11a,b]

We have previously studied the reaction of aliphatic amines with epoxides in the presence of catalytic amounts of samarium diiodide to produce β-aminoalcohols. We have now extended this study to the ring opening of cyclic epoxides by aromatic amines. Results are gathered in the Table 1. In a typical experiment, addition of the aromatic amine to 10% $SmI_2(THF)_2$ suspended in methylene chloride was followed by addition of the epoxide. Reactions of aniline and cyclohexene oxide were first examined and afforded the β-aminoalcohol as the *trans* isomer in good yield without the formation of side products after one night at room temperature (entry 1). Decreasing the catalytic ratio to 5% did not bring any modification in the yield in reaction product (70%). We then tested the reaction of various aromatic amines substituted by electron donating or withdrawing groups (entries 2–4) to obtain the corresponding β-aminoalcohols in satisfactory yields. The reaction of other cyclic epoxides, cyclohexadiene monoxide **1b** and cyclopentene epoxide **1c** with aniline and substituted anilines afforded similarly the corresponding *trans* β-aminoalcohols except for *p*-nitroaniline. Yet, the reaction of aniline with cycloheptene oxide afforded only small amounts (<10%) of the corresponding β-aminoalcohol after 24 h.



Keywords: Samarium diiodide; Lanthanides; Epoxides ring opening; β-Aminoalcohol; Enantioselective catalysis.

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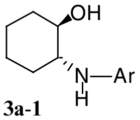
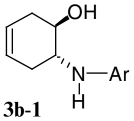
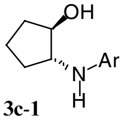
Table 1. Ring opening of *meso*-epoxides catalyzed by samarium diiodide

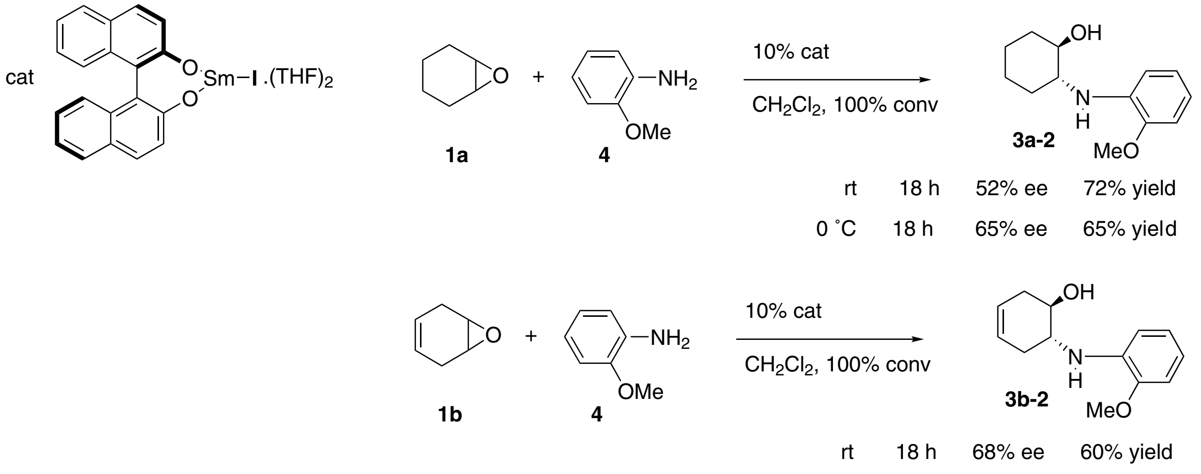
Entry	Epoxide	Amine	Product	Yield[a,b]
				
1	**1a**	Aniline	**3a-1**	75
2	**1a**	*o*-Anisidine	**3a-2**	75
3	**1a**	*p*-Anisidine	**3a-3**	57
4	**1a**	*p*-Bromoaniline	**3a-4**	76
				
5	**1b**	Aniline	**3b-1**	80
6	**1b**	*o*-Anisidine	**3b-2**	72
7	**1b**	*p*-Anisidine	**3b-3**	75
8	**1b**	*p*-Bromoaniline	**3b-4**	93
9	**1b**	*p*-Nitroaniline	**3b-5**	0
				
10	**1c**	Aniline	**3c-1**	50
11	**1c**	*o*-Anisidine	**3c-2**	61
11	**1c**	*p*-Anisidine	**3c-3**	63
12	**1c**	*p*-Bromoaniline	**3c-4**	78

[a] % in isolated product. Typical procedure: a solution of *o*-anisidine (276 mg, 2.2 mmol) in 5 mL CH_2Cl_2 is transferred under argon on a suspension of $SmI_2(THF)_2$ (110 mg, 0.2 mmol).[11e] Cyclohexene oxide (200 µL, 2 mmol) is then added with a syringe. The reaction medium is stirred for 18 h at room temperature and quenched by a hydrochloric acid solution (1 M) followed by a neutralization. After extraction and drying, the residue is purified by flash chromatography on silica (cyclohexane/AcOEt: 80/20).

[b] All products have been precedently reported and have been characterized by NMR, IR, and MS spectroscopies.

Catalytic enantioselective ring opening of *meso*-epoxides has been a focus of interest as an efficient method to create two contiguous asymmetric centers. Efficient catalysts have been reported for reactions with various nucleophiles such as PhSH, PhOH, $TMSN_3$, TMSCN.[12] However, there are only a few reports concerning the enantioselective catalysis of the ring opening of epoxides by amines.[13] Titanium-binol catalysts afforded aminoalcohols with high asymmetric induction by reacting epoxides containing ketal groups with aliphatic amines.[13a] Two systems involving lanthanides and binaphthol catalyze the opening of cyclohexene oxide by aniline. Low enantiomeric excesses were first reported using lanthanide chlorides,[5g] while better inductions were observed with ytterbium triflate in the presence of binol.[13b] Shibasaki and co-workers developed a praseodymium complex, Pr(*R*)—binol—$PPh_3P{=}O$, which afforded the enantioselective ring opening of *meso*-epoxides with *p*-anisidine and applied this method to the formal synthesis of 4-demethoxydaunomycin.[13c] These results prompted us to report our first results concerning the enantioselective aminolysis of *meso*-epoxides.

We have precedently described the preparation of new lanthanide iodobinaphthoxides and their application for enantioselective Diels–Alder and iminoaldol reac-



tions.[14] We have now found that bis-binaphthoxy iodo samarium (prepared from samarium triiodide and bis potassium (*R*)-binaphthoxide) catalyzes the reaction of cyclohexene oxide and cyclohexadiene monoxide with *o*-anisidine, affording the corresponding β-aminoalcohols **3a-2** and **3b-2** in good yields and with, respectively, 52% and 68% enantiomeric excess at room temperature. Asymmetric induction is increased by lowering temperature. The enantioselective desymmetrization of various epoxides with aromatic amines catalyzed by lanthanide iodobinaphthoxides is currently under study.

Samarium diiodide allows to perform ring opening of epoxides by aromatic amines with good yields in mild conditions and these reactions can be extended to the enantioselective synthesis of β-aminoalcohols with chiral samarium iodides.

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References and notes

1. Rogers, G. A.; Parsons, S. M.; Anderson, D. C.; Nilsson, L. M.; Bahr, B. A.; Kornreich, W. D.; Kaufman, R.; Jacobs, R. S.; Kirtman, B. *J. Med. Chem.* **1989**, *32*, 1217–1230.
2. Ager, D. J.; Prakash, I.; Schaad, D. *Chem. Rev.* **1996**, *96*, 835–875.
3. Deyrup, J. A.; Moyer, C. L. *J. Org. Chem.* **1969**, *34*, 175–179.
4. Rajender Reddy, L.; Arjun Reddy, M.; Bhanumati, N.; Rama Rao, K. *Synlett* **2000**, 339–340.
5. (a) Iqbal, J.; Pandey, A. *Tetrahedron Lett.* **1990**, *31*, 575–576; (b) Duran Pachon, L.; Gamez, P.; van Brussel, J. J. M.; Reedijk, J. *Tetrahedron Lett.* **2003**, *44*, 6025–6027; (c) Chandrasekhar, S.; Ramachandar, T.; Jaya Prakash, S. *Synthesis* **2000**, 1817–1818; (d) Sabitha, G.; Kiran Kumar Reddy, G. S.; Bhashar Reddy, K.; Yadav, J. S. *Synthesis* **2003**, 2298–2300; (e) Chakraborti, A. K.; Kondaskar, A. *Tetrahedron Lett.* **2003**, *44*, 8315–8319; (f) Ollevier, T.; Lavie-Compin, G. *Tetrahedron Lett.* **2002**, *43*, 7891–7893; (g) Fu, X. L.; Wu, S. H. *Synth. Commun.* **1997**, 1677–1683; (h) Rajender Reddy, L.; Arjun Reddy, M.; Bhanumati, N.; Rama Rao, K. *Synthesis* **2001**, 831–832; (i) Zhao, P. Q.; Xu, L. W.; Xia, C. G. *Synlett* **2004**, 846–850; (j) Swamy, N. R.; Goud, T. V.; Reddy, S. M.; Krishnaiah, P.; Venkateswarlu, Y. *Synth. Commun.* **2004**, *34*, 724–727.
6. (a) Chini, M.; Crotti, P.; Favero, L.; Macchia, F.; Pineschi, M. *Tetrahedron Lett.* **1994**, *35*, 433–436; (b) Meguro, M.; Asao, N.; Yamamoto, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2597–2601; (c) Sekar, G.; Singh, V. K. *J. Org. Chem.* **1999**, *64*, 287–289; (d) Ollevier, T.; Lavie-Compin, G. *Tetrahedron Lett.* **2004**, *45*, 49–52; (e) Augé, J.; Leroy, F. *Tetrahedron Lett.* **1996**, *37*, 7715–7716.
7. Cossy, J.; Bellosta, V.; Hamoir, C.; Desmurs, J. R. *Tetrahedron Lett.* **2002**, *43*, 7083–7086.
8. Das, U.; Crousse, B.; Kesayan, V.; Bonnet-Delpon, D.; Bégué, J. P. *J. Org. Chem.* **2000**, *65*, 6749–6751.
9. Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Venkat Narsaiah, A. *Tetrahedron Lett.* **2003**, *44*, 1047–1050.
10. (a) Kobayashi, S. *Eur. J. Org. Chem.* **1999**, *22*, 15–27; (b) Kobayashi, S.; Sugiara, M.; Kitagawa, H.; Lam, W. W. L. *Chem. Rev.* **2002**, *102*, 2227–2302.
11. (a) Collin, J.; Giuseppone, N.; Van de Weghe, P. *Coord. Chem. Rev.* **1998**, *178–180*, 117–144; (b) Van de Weghe, P.; Collin, J. *Tetrahedron Lett.* **1995**, *36*, 1649–1652; (c) Giuseppone, N.; Van de Weghe, P.; Mellah, M.; Collin, J. *Tetrahedron* **1998**, *54*, 13129–13148; (d) Giuseppone, N.; Collin, J. *Tetrahedron* **2001**, *57*, 8989–8998; (e) Jaber, N.; Assié, M.; Fiaud, J.-C.; Collin, J. *Tetrahedron* **2004**, *60*, 3075–3083; (f) Gil, R.; Eternot, M.; Guillerez, M.-G.; Collin, J. *Tetrahedron* **2004**, *60*, 3085–3090.
12. (a) Iida, T.; Yamamoto, N.; Sasai, H.; Shibazaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 4783–4784; (b) Matsunaga, S.; Das, J.; Roels, J.; Vogl, E. M.; Yamamoto, N.; Iida, T.; Yamaguchi, K.; Shibazaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 2252–2260; (c) Schaus, S. E.; Jacobsen, E. N. *Org. Lett.* **2000**, *2*, 1001–1004; (d) Zhu, C.; Yuan, F.; Gu, W.; Pan, Y. *Chem. Commun.* **2003**, *22*, 692–693.
13. (a) Sagawa, S.; Abe, H.; Hase, Y.; Inaba, T. *J. Org. Chem.* **1999**, *64*, 4962–4965; (b) Hou, X. L.; Wu, J.; Dai, L. X.; Xia, L. J.; Tang, M. H. *Tetrahedron: Asymmetry* **1998**, 1747–1752; (c) Sekine, A.; Oshima, T.; Shibazaki, M. *Tetrahedron* **2002**, *58*, 75–82.
14. (a) Collin, J.; Carrée, F.; Giuseppone, N.; Santos, I. *J. Mol. Catal. A* **2003**, *200*(1–2), 185–189; (b) Jaber, N.; Carrée, F.; Fiaud, J. C.; Collin, J. *Tetrahedron: Asymmetry* **2003**, 2067–2071.