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HIGHLY REGIOSELECTIVE REARRANGEMENT OF 2,3-DIARYL-OXIRANES INTO 2,2-DIARYLACETALDEHYDES CATALYZED BY YTTERBIUM PORPHYRIN COMPLEX, Yb(TPP)OTf

Toshikatsu Takanami,* Shin-ichiro Nakajima, Shoichi Nakadai, Fumio Hino, and Kohji Suda*

Meiji Pharmaceutical University, 2-522-1, Noshio, Kiyose, Tokyo 204-8588, Japan
e-mail: takanami@my-pharm.ac.jp; suda@my-pharm.ac.jp

Abstract – [5,10,15,20-Tetraphenylporphyrinato]ytterbium(III) triflate, Yb(TPP)-OTf, is an efficient Lewis acid catalyst for the highly regioselective rearrangement of 2,3-diaryloxiranes into 2,2-diarylacetaldehydes. The catalytic process can be easily performed not only in dichloroethane but also in a more environmentally friendly solvent, benzotrifluoride.

INTRODUCTION

2,2-Diarylacetaldehydes are useful synthetic precursors of many biologically active natural and synthetic products that contain diarylmethane structural motifs.¹ Among numerous methods for the preparation of 2,2-diarylacetaldehydes,^{1,2} acid-promoted rearrangement of 2,3-diaryloxiranes constitutes one of the most straightforward strategies, and hence a number of different Lewis acid-catalyzed methods have been developed for this purpose.^{3,4} However, most of these developed methods appear to suffer from lack of regioselectivity, usually affording a mixture of 2,2-diarylacetaldehydes and their regioisomeric products, 1,2-diarylethanones, and reduced yields of the desired aldehydes are therefore often obtained. Thus, there is a need to develop an alternative catalyst to promote such rearrangement with higher efficiency and regioselectivity.

Our laboratory has recently developed iron(III) and chromium(III) porphyrin complexes (Figure 1) as a new family of highly regio- and stereoselective Lewis acid catalysts for the ring-opening rearrangement of various epoxides, including α,β -epoxy silyl ethers, α,β -epoxy enones, and monoalkyl-substituted epoxides, to the corresponding carbonyl compounds.^{5,6} This paper describes the efficient rearrangement of 2,3-diaryloxiranes **1** to 2,2-diarylacetaldehydes **2** that proceeds with high levels of yields and regio-

selectivity using a new porphyrin-based Lewis acid catalyst, [5,10,15,20-tetraphenylporphyrinato]-ytterbium(III) triflate, Yb(TPP)OTf. Another advantage of the method is that the reported rearrangements using the Yb(TPP)OTf catalyst system can be easily performed in benzonitrile (BTF),⁷ which has recently emerged as a useful alternative solvent for organic reactions currently conducted in dichloromethane (DCM) and related solvents, without deterioration in yields and regioselectivity. This is considered of increasing importance as greener processes are sought because of environmental concerns.

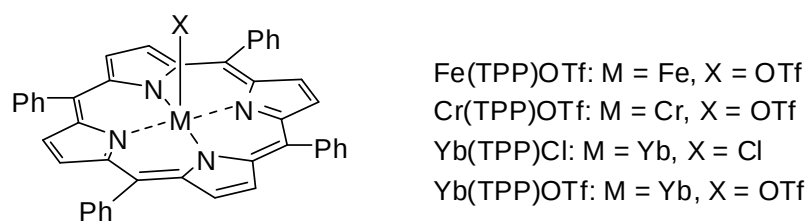


Figure 1. Structures of porphyrin-based Lewis acid catalysts

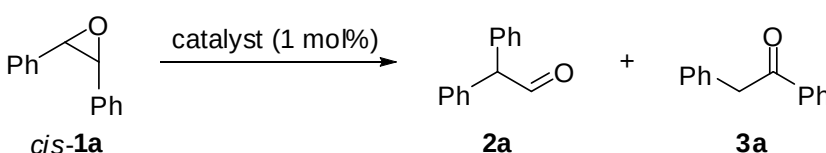
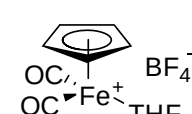
RESULTS AND DISCUSSION

cis-Stilbene oxide *cis*-**1a** was chosen as a test substrate in the initial experiments to optimize the reaction conditions, because *cis*-2,3-diaryloxiranes often provide lower regioselectivity than the *trans* isomers in Lewis acid-promoted rearrangements.^{3a,3c} Thus, we evaluated various Lewis acid catalysts in the rearrangement of model substrate *cis*-**1a**, and the results are illustrated in Table 1. When we attempted the rearrangement of *cis*-**1a** with 1 mol% of porphyrin-based Lewis acid catalysts, Fe(TPP)OTf and Cr(TPP)OTf, in dichloroethane (DCE) at 83 °C, we obtained the corresponding aldehyde **2a** in only moderate yields along with substantial amounts of undesired isomeric ketone **3a** (entries 1 and 2). Other Lewis acids, such as Er(OTf)₃,^{3a} Yb(OTf)₃, Bi(O)ClO₄,^{3b} Bi(OTf)₃,^{3c} and [(η⁵-C₅H₅)Fe(CO)₂(THF)]BF₄,^{3d} most of which are known as effective Lewis acid catalysts for the rearrangement of epoxides to carbonyl compounds, also gave unsatisfactory results to obtain moderate yields of the desired aldehyde **2a** (entries 7–11). In the case with InCl₃,^{3e} no reaction occurred to recover the starting epoxide *cis*-**1a** (entries 12 and 13).⁸ Despite these discouraging results, we recognized that lanthanide- and bismuth-based Lewis acids can afford slightly higher regioselectivity compared to the porphyrin-based Lewis acid catalysts (cf. entries 1, 2, and 7–10), and hence we assumed that the use of metalloporphyrin complexes possessing such central metal ions as Er(III), Yb(III), and Bi(III) as catalysts might improve the regioselectivity of the reaction. Among these porphyrin complexes, Yb(III)-containing complexes have been well-characterized with regard to their structures and physical properties, and several efficient methods for their preparation are available in the literature.⁹ Therefore, we chose Yb(TPP)Cl and Yb(TPP)OTf as porphyrin-based Lewis acid catalysts, and assessed their catalytic ability toward the rearrangement of

cis-**1a**. Indeed, while Yb(TPP)Cl could not promote the rearrangement (entry 3), treatment of epoxide *cis*-**1a** with 1 mol% of Yb(TPP)OTf in DCE at 83 °C resulted in a highly regioselective rearrangement to afford 89% yield of the desired aldehyde **2a** along with only a trace amount (<5%) of ketone **3a** (entry 4). Further optimization revealed that DCE was the optimal solvent (entries 4–6).

Using the optimal conditions, we next explored the scope and generality of the procedure (Table 2). As a whole, the Yb(TPP)OTf catalyst system could easily be applied to various 2,3-diaryloxiranes such as those having phenyl, naphthyl, and biphenyl moieties. Regardless of whether the stereochemistry of a substrate is *cis* or *trans*, excellent yields and high regioselectivity are typically obtained (entries 1 and 2). Thus, this catalytic protocol can obviate the need for careful separation of the *cis* and *trans* isomers of

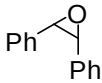
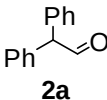
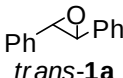
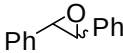
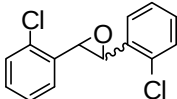
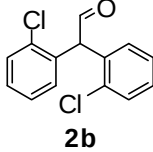
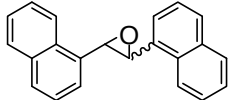
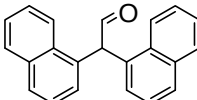
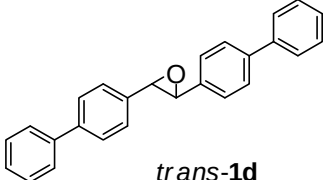
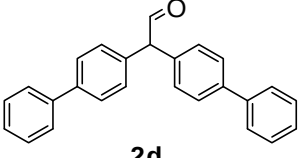
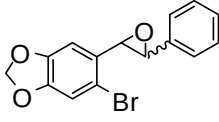
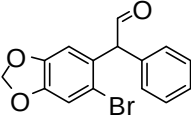
Table 1. Lewis acid-catalyzed rearrangement of *cis*-stilbene oxide *cis*-**1a**

				
entry	catalyst	conditions solvent/temp/time	yield (%) ^a of 2a	yield (%) ^a of 3a
1	Fe(TPP)OTf	DCE/83 °C/1 h	73	23
2	Cr(TPP)OTf	DCE/83 °C/3 h	66	32
3	Yb(TPP)Cl	DCE/83 °C/12 h	no reaction	
4	Yb(TPP)OTf	DCE/83 °C/4 h	89	<5
5	Yb(TPP)OTf	dioxane/100 °C/2 h	55	21
6	Yb(TPP)OTf	toluene/110 °C/6 h	44	21
7	Er(OTf) ₃	DCM/rt/2 h	73	15
8	Yb(OTf) ₃	DCM/rt/1 h	62	16
9	Bi(O)ClO ₄	DCM/rt/10 h	69	13
10	Bi(OTf) ₃	DCM/rt/1 h	74	13
11		DCM/rt/15 h	75	15
12	InCl ₃	THF/50 °C/24h	no reaction	
13	InCl ₃	DCM/40 °C/24h	no reaction	

a) Isolated yield.

2,3-diaryloxiranes prior to using these epoxides as the substrates in the rearrangement. For example, subjecting 1 mol% of Yb(TPP)OTf to a 1:1 mixture of *cis*- and *trans*-**1a** led to the formation of aldehyde **2a** as the major product, the yield of which (87%) was comparable to that obtained from the corresponding single isomers (entry 3). Similar results were obtained for epoxides **1b** and **1c** that consist of their *cis* and *trans* isomers (entries 4 and 5). As expected, biphenyl-substituted derivative *trans*-**1d** could easily be converted to the corresponding aldehyde **2d**, a useful synthetic intermediate for a clay mimic organic host,¹⁰ in a high yield (entry 6). The asymmetrical epoxide **1e** that possesses different aryl substituents on the oxirane ring also proved to be a suitable substrate for this catalytic rearrangement, fur-

Table 2. Yb(TPP)OTf-catalyzed rearrangement of 2,3-diaryloxirane to 2,2-diaryl-acetaldehyde^a

entry	substrate	time (h)	product	yield (%) ^b
1	 <i>cis</i> - 1a	4	 2a	89
2	 <i>trans</i> - 1a	4	2a	94
3	 1a (<i>cis/trans</i> = 1:1)	4	2a	87
4	 1b (<i>cis/trans</i> = 1:1)	12	 2b	90
5	 1c (<i>cis/trans</i> = 1:1)	4	 2c	87
6	 <i>trans</i> - 1d	5	 2d	85
7	 1e (<i>cis/trans</i> = 1:1)	12	 2e	92

a) Conditions: Yb(TPP)OTf (1 mol%), DCE, 83 °C. b) Isolated yield.

nishing the desired aldehyde **2e** in 92% yield (entry 7). In all cases, only trace amounts (<5%) of undesired isomeric ketones could be detected in the $^1\text{H-NMR}$ spectra of the crude reaction mixtures.

We next turned our attention to the use of BTF as a solvent in place of DCE. As briefly mentioned above, BTF is a potential substitute for DCM and related solvents mainly because of its higher boiling point and lower toxicity, and its use as reaction media in preparative organic chemistry and homogeneous catalysis is a topic of ongoing interest.⁷ However, Lewis acid-mediated reactions in BTF are still limited since BTF is somewhat labile toward Lewis acidic conditions; for example, the CF_3 group of BTF is known to react with strong Lewis acids such as AlCl_3 even at ambient temperature.⁷ Thus, development of a new, milder Lewis acid catalyst that can be used in BTF is highly desirable. As illustrated in Table 3, the $\text{Yb}(\text{TPP})\text{OTf}$ -catalyzed rearrangement of *cis*-**1a** occurred in refluxing BTF with yield and regioselectivity fully comparable to those obtained from the counterpart reaction in DCE (entry 1, cf. entry 4 in Table 1), whereas other catalysts, such as $\text{Er}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$, $\text{Bi}(\text{OTf})_3$, $\text{Bi}(\text{O})\text{ClO}_4$, and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]\text{BF}_4$, all of which did not work well in BTF, produced significant erosion of yields and regioselectivity as well as prolonged reaction time (entries 2–6). The present conditions using the $\text{Yb}(\text{TPP})\text{OTf}$ catalyst and BTF as a solvent translated smoothly to other 2,3-diaryloxiranes (Table 4). As expected, all the substrates examined readily undergo the rearrangement to afford the corresponding 2,2-diarylacetaldehydes in high yields. More noteworthy was the observation that the yields of these reactions

Table 3. Lewis acid-catalyzed rearrangement of *cis*-stilbene oxide *cis*-**1a** in BTF

entry	catalyst	temp (°C)	time (h)	yield (%) ^a of 2a	yield (%) ^a of 3a
1	$\text{Yb}(\text{TPP})\text{OTf}$	102	3	87	<5
2	$\text{Er}(\text{OTf})_3$	rt	10	51	20
3	$\text{Yb}(\text{OTf})_3$	rt	9	50	20
4	$\text{Bi}(\text{O})\text{ClO}_4$	rt	24	40	12
5	$\text{Bi}(\text{OTf})_3$	rt	5	51	17
6		rt	24	46	18

a) Isolated yield.

in BTF are generally higher than those of the parallel reactions performed in DCE (cf. Table 2). These results clearly show that BTF can be employed as an excellent replacement for DCE in Yb(TPP)OTf-catalyzed rearrangements.

Table 4. Yb(TPP)OTf-catalyzed rearrangement of 2,3-diaryloxirane to 2,2-diarylacetaldehyde in BTF^a

entry	substrate	time (h)	product	yield (%) ^b
1	<i>cis</i> - 1a	3	2a	87
2	1a (<i>cis/trans</i> = 1:1)	3	2a	91
3	1b (<i>cis/trans</i> = 1:1)	12	2b	93
4	1c (<i>cis/trans</i> = 1:1)	5	2c	90
5	<i>trans</i> - 1d	6	2d	88
6	1e (<i>cis/trans</i> = 1:1)	12	2e	93

a) Conditions: Yb(TPP)OTf (1 mol%), BTF, 102 °C. b) Isolated yield.

CONCLUSION

In summary, we have developed a new class of porphyrin-based Lewis acid catalyst, Yb(TPP)OTf, that can efficiently promote highly regioselective rearrangement of 2,3-diaryloxiranes to 2,2-diarylacetaldehydes. This rearrangement was successfully carried out in DCM but could also be performed in the more environmentally friendly solvent BTF. Mechanistic investigations and applications of this class of catalysts to new transformations are currently underway.

EXPERIMENTAL

General ¹H- and ¹³C-NMR spectra were recorded on a JEOL JNM-AL300 spectrometer. The chemical shifts were reported in ppm relative to CHCl₃ (δ = 7.24) for ¹H-NMR and relative to the central resonance of CDCl₃ (δ = 77.0) for ¹³C-NMR. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer. UV-visible absorption spectra were measured with a Hitachi U-3210 spectrophotometer. Dichloroethane (DCE) and dichloromethane (DCM) were distilled under argon from CaH₂. Benzotrifluoride (BTF) was distilled under argon from P₂O₅. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Kanto Kagaku Silica Gel 60 (spherical) and Merck kiesel-gel 60 F254 were employed for silica gel column and thin layer chromatography, respectively. Both *cis*- and *trans*-stilbene oxides, *cis*-**1a** and *trans*-**1a**, were purchased from Aldrich. Other 2,3-diaryloxiranes **1b–e** were prepared as described in the

literature.^{1d,4a,11} Porphyrin-based catalysts, Cr(TPP)OTf and Fe(TPP)OTf, were prepared by the literature methods.^{5d} Unless otherwise stated, all commercially available chemicals were used without further purification.

Preparation of [5,10,15,20-tetraphenylporphyrinato]ytterbium(III) chloride [Yb(TPP)Cl]⁹

A 300 mL three necked flask equipped with a magnetic stirring bar, a reflux condenser, and rubber septa was charged with 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine [H₂TPP] (1.0 g, 1.6 mmol) and 1-chloronaphthalene (150 mL). The mixture was stirred at 150 °C for 30 min to dissolve the porphyrin. To the solution was added YbCl₃·6H₂O (1.0 g, 2.6 mmol), and the mixture was refluxed until the Soret band of the free base porphyrin was replaced by that of the ytterbium porphyrin complex at 416 nm. The reaction mixture was allowed to cool to rt and then concentrated under a reduced pressure. The resulting residue was dissolved in 10 mL of pyridine, and the solution was poured into ice-cooled water (300 mL). The resulting precipitate was collected by filtration and washed with copious amounts of water to give the pyridine-coordinated ytterbium porphyrin complex. The complex was recrystallized from CH₂Cl₂/hexane (twice times) and dried in a vacuum oven for 48 h at 150 °C under a reduced pressure (1 mmHg) to give the pyridine-free Yb(TPP)Cl complex (806 mg, 60%). UV/vis (CH₂Cl₂): λ_{max} (log ε): 416 (5.4), 552 (4.2) nm; Anal. Calcd for C₄₄H₂₈ClN₄Yb·H₂O: C, 62.97; H, 3.60; N, 6.68. Found: C, 63.52; H, 3.49; N, 6.66.

Preparation of [5,10,15,20-tetraphenylporphyrinato]ytterbium(III) triflate [Yb(TPP)OTf]

A flame-dried 50 mL two necked flask equipped with a magnetic stirring bar, a reflux condenser, and rubber septa was charged with Yb(TPP)Cl (100 mg, 0.12 mmol) and AgOTf (30 mg, 0.15 mmol). The reaction vessel was evacuated and flushed with argon (three times), and absolute THF (25 mL) was added. The mixture was refluxed under argon for 10 h, allowed to reach rt, and concentrated under a reduced pressure. The residue was dissolved in CH₂Cl₂ (ca. 30 mL), and filtered through a pad of Celite. The filtrate was concentrated under a reduced pressure. The resulting solid was recrystallized from CH₂Cl₂/hexane (twice times) and dried in a vacuum oven for 24 h at 100 °C under a reduced pressure (1 mmHg) to give Yb(TPP)OTf (97 mg, 85%). UV/vis (CH₂Cl₂): λ_{max} (log ε): 418 (5.5), 549 (4.2) nm; Anal. Calcd for C₄₅H₂₈F₃N₄O₃SYb·H₂O: C, 56.72; H, 3.17; N, 5.88. Found: C, 56.94; H, 3.25; N, 5.60.

General procedure for the Yb(TPP)OTf-catalyzed rearrangement of 2,3-diaryloxiranes to 2,2-diarylacetaldehydes

To a solution of 2,3-diaryloxirane **3** (0.5 mmol) in DCE or BTF (5 mL) was added Yb(TPP)OTf (4.8 mg, 0.005 mmol). The mixture was refluxed under argon. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under a reduced pressure. The residue was passed through a silica gel short column (1:3 AcOEt–hexane) to remove the catalyst. The eluate was concentrated in vacuo, and the residue was chromatographed on silica-gel (1:9 AcOEt–hexane) to give 2,2-diarylacetaldehyde **2**.

The aldehydes, **2a**,¹² **2c**,^{4a} and **2e**,^{1d} are known compounds and easily characterized by comparison with authentic samples.

2,2-Diphenylacetaldehyde (2a) ¹H-NMR (CDCl₃, 300 MHz) δ : 9.94 (1H, d, J = 2.5 Hz), 7.40-7.14 (10H, m), 4.88 (1H, d, J = 2.5 Hz).

2,2-Bis(2-chlorophenyl)acetaldehyde (2b) ¹H-NMR (CDCl₃, 300 MHz) 9.93 (1H, d, J = 0.5 Hz), 7.48-7.45 (2H, m), 7.31-7.22 (4H, m), 7.04-6.97 (2H, m), 5.84 (1H, brs); ¹³C NMR (CDCl₃, 100 MHz): δ 197.1, 135.1, 133.4, 130.5, 130.2, 129.2, 127.1, 58.3; IR (KBr): 3737, 1720, 1651, 1516, 1469, 1045, 748, 671 cm⁻¹; HRMS (EI) m/z : calcd for C₁₄H₁₀Cl₂O: 264.0109, found: 264.0107.

2,2-Di(naphthalen-1-yl)acetaldehyde (2c) ¹H-NMR (CDCl₃) δ : 10.22 (1H, d, J = 2.1 Hz), 7.92-7.7.89 (4H, m), 7.53-7.38 (6H, m), 7.24-7.19 (4H, m), 6.37 (1H, d, J = 2.1 Hz).

2,2-Di(biphenyl-4-yl)acetaldehyde (2d) ¹H-NMR (CDCl₃) δ : 10.01 (1H, d, J = 2.2 Hz), 7.73-7.31 (18H, m), 4.97 (1H, d, J = 2.2 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 198.3, 140.7, 140.5, 135.2, 130.7, 129.6, 128.8, 127.8, 127.1, 63.5; IR (KBr): 3737, 1701, 1647, 1516, 1115, 675, 671 cm⁻¹; HRMS (EI) m/z : calcd for C₂₆H₂₀O: 348.1514, found: 348.1516.

2-(6-Bromobenzo[d][1,3]dioxol-5-yl)-2-phenylacetaldehyde (2e) ¹H-NMR (CDCl₃) δ : 9.91 (1H, d, J = 0.9 Hz), 7.40-7.19 (5H, m), 7.06 (1H, s), 6.57 (1H, s), 5.95 (1H, d, J = 3.9 Hz), 5.94 (1H, d, J = 3.9 Hz), 5.39 (1H, brs).

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