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Metalloporphyrin-catalyzed regioselective rearrangement of monoalkyl-substituted epoxides into aldehydes

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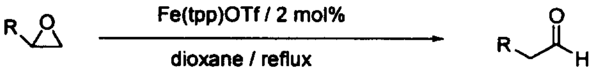
Abstract

Iron(III) tetraphenylporphyrin, Fe(tpp)OTf, is an efficient catalyst for the regioselective rearrangement of simple monoalkyl-substituted epoxides into the corresponding aldehydes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: iron(III) tetraphenylporphyrin triflate; monoalkyl-substituted epoxide; rearrangement; aldehyde.

Epoxides are one of the most versatile classes of organic compounds owing to their high reactivity. Among epoxide-transformations, the rearrangement of epoxides such as those bearing aryl-, vinyl-, silyl-, and trialkyl-substituents to carbonyl compounds is a well-investigated reaction, and leading references can be found in several reviews and articles.[1,2] However, less commonly observed are isomerization reactions of epoxides having a simple monoalkyl-substituent to the corresponding aldehydes and/or methyl ketones.[3–5] In particular, reports on a regioselective catalytic version of the isomerization to aldehydes are very limited.[4,5] In the course of our general research program directed toward the development of novel and synthetically useful chemical properties of metalloporphyrins, we have recently found that a high-valent metalloporphyrin works as a mild and characteristic Lewis acid catalyst in the rearrangement of small-ring heterocycles.[6] This communication describes that monoalkyl-substituted epoxides (**1**) are effectively isomerized to aldehydes (**2**) by iron(III) tetraphenylporphyrin triflate, Fe(tpp)OTf, catalysis in a highly regioselective manner (Scheme 1).



Scheme 1.

Table 1 shows the results of rearrangement of 1,2-epoxydecane (**1a**) with Lewis acids. All attempts with conventional Lewis acids such as $BF_3 \cdot OEt_2$, $TiCl_4$ and $MgBr_2 \cdot OEt_2$ in a catalytic (5 mol%) and an equimolar amount in dichloromethane were unsuccessful; no reaction occurred (runs 2, 4 and 6) or gave

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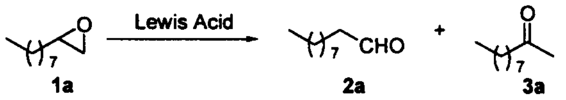
Table 1
Lewis acid-mediated rearrangement of epoxide **1a**



Run	Lewis acid (mol%)	Conditions solvent / time / temp	Yield (%)[a] (2a/3a)[b]
1	$BF_3 \cdot OEt_2$ (100)	CH_2Cl_2 / 0.5h / 0°C	complex mixture
2	$BF_3 \cdot OEt_2$ (5)	CH_2Cl_2 / 24h / 0°C→ r.t.	no reaction
3	$TiCl_4$ (100)	CH_2Cl_2 / 0.5h / 0°C	complex mixture
4	$TiCl_4$ (5)	CH_2Cl_2 / 24h / 0°C→ r.t.	no reaction
5	$MgBr_2 \cdot OEt_2$ (100)	CH_2Cl_2 / 0.5h / 0°C	complex mixture
6	$MgBr_2 \cdot OEt_2$ (5)	CH_2Cl_2 / 24h / 0°C→ r.t.	no reaction
7	Fe(tpp)OTf (2)	$ClCH_2CH_2Cl$ / 4.5h / reflux	93 (93/7)
8	Fe(tpp)OTf (2)	dioxane / 1.5h / reflux	~100 (96/4)
9	Fe(tpp)OTf (2)	toluene / 3h / reflux	~100 (94/6)
10	$Fe(tpp)ClO_4$ (2)	dioxane / 8h / reflux	79[c] (93/7)

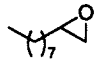
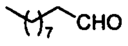
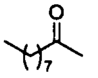
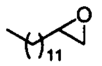
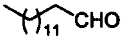
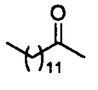
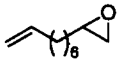
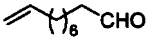
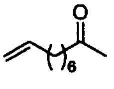
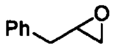
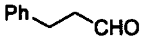
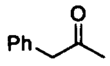
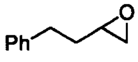
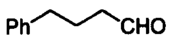
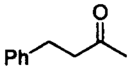
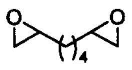
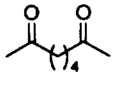
[a] Isolated yield.
[b] Isomer ratios were determined by 270MHz ^{1}H-NMR analysis of the crude reaction mixture.
[c] 15% of **1a** was recovered.

only inseparable complex mixtures (runs 1, 3 and 5). On the other hand, iron(III) tetraphenylporphyrin complexes with sufficient Lewis acidity showed a unique behavior for the rearrangement of **1a**.[7] When **1a** was treated with a catalytic amount of Fe(tpp)OTf (2 mol%) in refluxing 1,2-dichloroethane for 4.5 h, the corresponding aldehyde **2a** was obtained in high yield along with a small amount of methylketone **3a** (run 7). The total yield and the ratio of **2a** and **3a** were 93% and 93/7, respectively. This catalytic rearrangement also took place smoothly in various solvents with practical regioselectivity (runs 7–9), and the reaction in dioxane gave the most satisfactory result with respect to the yield, reaction time and the isomer ratio of **2a** and **3a** (run 8). The same rearrangement with $Fe(tpp)ClO_4$ (2 mol%) was, on the other hand, incomplete in dioxane; 15% of the starting material was recovered after an 8 h reaction (run 10).

We then examined the generality of the Fe(tpp)OTf-catalyzed rearrangement with various monoalkyl-substituted epoxides (**1a**–**1f**) in refluxing dioxane.[8] The results are summarized in Table 2. The total yield and regioselectivity of the products in the rearrangement were independent of the chain length of the epoxides used, and **1a** and **1b** were quantitatively converted to the corresponding aldehydes, **2a** and **2b**, respectively. The presence of a phenyl group or a terminal double bond in the substrates essentially showed no effect on the regioselectivity of the rearrangement: epoxides **1c**–**1e** were regioselectively converted to the corresponding aldehydes **2c**–**2e** in satisfactory yields. Diepoxide **1f** also underwent the catalytic isomerization without an increased amount of catalyst under the same conditions. Again, the yield and chemoselectivity of dialdehyde **2f** were excellent. Although we have not yet studied the mechanism of this rearrangement, the rationale for the formation of aldehydes **2** is as follows: an electrophilic attack of metalloporphyrin, Fe(tpp)OTf, toward the oxygen atom of epoxides **1** brings about the C–O bond cleavage to give the more stable carbocation, i.e., a secondary carbocation. The subsequent 1,2-shift of a hydride from the terminal carbon affords aldehyde **2**.

In summary, we have shown that Fe(tpp)OTf can effectively catalyze the regioselective rearrangement

Table 2
Fe(tpp)OTf-catalyzed rearrangement of epoxides **1** to aldehydes **2**

Run	Substrate	Products		Yield (%)^{a} (2 / 3)^{b}
1	 **1a**	 **2a**	 **3a**	~100 (96/4)
2	 **1b**	 **2b**	 **3b**	~100 (95/5)
3	 **1c**	 **2c**	 **3c**	~100 (94/6)
4	 **1d**	 **2d**	 **3d**	~100 (94/6)
5	 **1e**	 **2e**	 **3e**	~100 (94/6)
6	 **1f**	 **2f**	 **3f**	98 (97/3)

[a] Isolated yield.

[b] Isomer ratios were determined by 270MHz ^{1}H-NMR analysis of the crude reaction mixture.

of monoalkyl-substituted epoxides **1** to the corresponding aldehydes **2**. Compared to other reagents reported so far for the rearrangement of **1** to **2**,[4,5] the Fe(tpp)OTf catalyst has several advantages as follows: (1) this stable, crystalline solid is more convenient to handle; (2) only a catalytic amount of Fe(tpp)OTf (<2 mol%) is required for the rearrangement; and (3) high yields and almost complete regioselectivity can easily be achieved by this metalloporphyrin catalyst. We are further investigating the scope, mechanism, and synthetic utility of this potentially useful reaction.

Acknowledgements

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8. General procedure: A solution of an epoxide **1** (1 mmol) and Fe(tpp)OTf (0.02 mmol) in dioxane (3 ml) was refluxed under N_2 until the starting material was no longer detectable by TLC (1.5–6.5 h). The solvent was removed by evaporation and the resulting residue was purified by a florisil short column (EtOAc) to give the corresponding aldehyde **2**. All the products gave satisfactory NMR, IR and high resolution mass spectra. For example, ^1H and ^{13}C NMR data of dialdehyde **2f** are as follows. ^1H NMR (270 MHz, $CDCl_3$) δ: 9.77 (2H, t, J=1.7 Hz), 2.44 (4H, dt, J=1.7 and 7.3 Hz), 1.63 (4H, m), 1.41–1.30 (4H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ: 202.6, 43.8, 28.9, 21.8.