Cite this: Chem. Commun., 2011, 47, 10963-10965

## COMMUNICATION

## Selective oxidation of terminal aryl and aliphatic alkenes to aldehydes catalyzed by iron(III) porphyrins with triflate as a counter anion<sup>†</sup>

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*Received 16th June 2011, Accepted 25th August 2011* DOI: 10.1039/c1cc13574k

[Fe(Por)CF<sub>3</sub>SO<sub>3</sub>] (Por = porphyrin dianion) can efficiently catalyze selective oxidation of terminal aryl alkenes and aliphatic alkenes to aldehydes in good to high yields under mild conditions.

Aldehyde is frequently used in organic synthesis.<sup>1</sup> Traditional methods for the synthesis of aldehyde mainly rely on oxidation of alcohol and reduction of ester.<sup>1,2</sup> As many alkenes can be obtained directly from petrochemicals, the conversion of alkene to aldehyde by oxidation (Wacker-type reaction) and hydroformylation is of great interest in both academia and industry.<sup>3,4</sup> Wacker oxidation is a well-known reaction that converts alkenes to carbonyl compounds using palladium catalysts.<sup>4</sup> Its most significant industrial application is the conversion of ethylene to acetaldehyde. However, when terminal alkenes except ethylene are employed as substrates, methyl ketones instead of aldehydes are obtained as the main products. Although some modified Wacker oxidation reactions have been developed, they either give a mixture of ketones and aldehydes, or require a directing group such as heteroatom(s) installed in substrates for chelation with palladium.<sup>5</sup> Recently, we reported that ruthenium porphyrin efficiently and selectively catalyzes 'Wacker-type' oxidation of terminal alkenes to aldehydes through a tandem epoxidation-isomerization (E-I) pathway, but the alkenes are confined to styrenes and cinnamenyl alkenes, and aliphatic alkenes were found to be poor substrates for the ruthenium catalysis.<sup>6</sup> As part of our program to develop sustainable catalysis, we herein describe a selective 'Wackertype' oxidation of terminal alkenes to aldehydes catalyzed by iron(III) porphyrins. Importantly, both aryl and aliphatic alkenes can be selectively oxidized to aldehydes when  $[Fe(Por)CF_3SO_3]$ (Por = porphyrin dianion) is used as the catalyst.

At the outset, we examined the oxidation of styrene with PhIO using  $[Fe(2,6-Cl_2TPP)Cl]$  [2,6-Cl\_2TPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin] as the catalyst.<sup>7</sup> Treatment of styrene with PhIO (1.5 equiv.) in the presence of a catalytic amount of  $[Fe(2,6-Cl_2TPP)Cl]$  (2 mol%) in dichloromethane at room temperature afforded styrene oxide without phenylacetaldehyde being detected (Table 1, entry 1).

As iron(III) porphyrin with a weakly coordinating anion as the axial ligand would have strong Lewis acidity that is needed for promoting isomerization of epoxide to aldehyde,<sup>8</sup> we tested the activity of [Fe(2,6-Cl<sub>2</sub>TPP)CF<sub>3</sub>SO<sub>3</sub>] towards this tandem E–I reaction. [Fe(2,6-Cl<sub>2</sub>TPP)CF<sub>3</sub>SO<sub>3</sub>] (generated *in situ* by reacting [Fe(2,6-Cl<sub>2</sub>TPP)CI] with AgSO<sub>3</sub>CF<sub>3</sub>) catalysed the E–I reaction of styrene with PhIO to give phenylacetaldehyde in 62% yield along with 5% yield of benzaldehyde, no epoxide was observed (Table 1, entry 2). Replacing CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> by other anions such as ClO<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, and PF<sub>6</sub><sup>-</sup> afforded similar

**Table 1** The iron(III) porphyrins catalyzed E–I reaction of styrene to phenylacetaldehyde<sup>a</sup>

Ph → Ia [Fe(Por)CI] (2 mol%) AgX(2 mol%) PhIO, DCM, RT Ph → CHO + Ph → CHO + Ph → CHO 2a Ph → 2b Ph → CHO

				Yie	ld <sup>b</sup> (	%)
Entry <sup>a</sup>	[Fe(Por)Cl]	AgX	Conversion <sup><math>b</math></sup> (%)	2a	2b	2c
1	[Fe(2,6-Cl <sub>2</sub> TPP)Cl]	_	100		60	5
2	[Fe(2,6-Cl <sub>2</sub> TPP)Cl]	AgOTf	100	62		5
3	[Fe(2,6-Cl <sub>2</sub> TPP)Cl]	AgClO <sub>4</sub>	100	60		3
4	[Fe(2,6-Cl <sub>2</sub> TPP)Cl]	AgSbF <sub>6</sub>	100	43		8
5	[Fe(2,6-Cl <sub>2</sub> TPP)Cl]	AgPF <sub>6</sub>	97	41		10
6	[Fe(F <sub>20</sub> -TPP)Cl]	AgOTf	40	37		
7	[Fe(TTP)Cl]	AgOTf	3	3		
8	[Fe(TPP)Cl]	AgOTf	39	3	30	5
9		AgOTf	_			

<sup>*a*</sup> 0.2 mmol styrene, PhIO (0.3 mmol), catalyst (2 mol%) and silver salts (2 mol%) were mixed in 2 mL DCM and stirred at room temperature for 8 hours. <sup>*b*</sup> Determined by GC with *n*-dodecane as the internal standard.



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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures, compound characterization see DOI: 10.1039/c1cc13574k

results (entries 3–5). The other iron porphyrins with triflate anion generated *in situ* gave lower substrate conversions (entries 6–8). Presumably this is due to the oxidative instability of  $[Fe(TPP)]^+$  and in the case of  $[Fe(F_{20}-TPP)]^+$ , the F substituents render the more oxidizing "putative  $[Fe(F_{20}-TPP)O]^+$ " intermediate less accessible. AgSO<sub>3</sub>CF<sub>3</sub> alone failed to catalyze the E–I reaction under the same conditions (Table 1, entry 9).

For easy operation,  $[Fe(2,6-Cl_2TPP)CF_3SO_3]$  was prepared according to the literature method.<sup>86</sup> The effects of solvent, temperature and substrate ratio were examined and the results are depicted in Table SII (see ESI†). The reaction in dichloromethane at room temperature with substrate ratio of styrene : PhIO = 3 : 1 gave best result and the byproduct benzaldehyde or epoxide was minimized (83% yield, Table SII†, entry 13). Excess styrene was found to lead to a higher yield of aldehyde. With other oxidants, such as *tert*-butylhydroperoxide, oxone or pyridine oxide, the reaction yield significantly dropped (see ESI†).

With the optimized conditions, we examined the scope of substrates for the [Fe(2,6-Cl<sub>2</sub>TPP) CF<sub>3</sub>SO<sub>3</sub>]-catalyzed E-I reaction of terminal alkenes to aldehydes. As depicted in Table 2, various aryl alkenes underwent the E-I reaction to give corresponding aldehydes in good to high yields. For examples, the reaction of both 4-methylstyrene 1b and 4-chlorostyrene 1d with PhIO gave corresponding aldehydes in 93% and 87% yields respectively (Table 2, entries 1 and 3). para-Methoxy substituents led to lower product yield (64% yield, entry 2). Varying the halo substituent(s) on the phenyl ring was found to have only a slight impact on the reaction with corresponding aldehydes obtained in 86-94% yields (entries 3-7). The 1,1-disubstituted alkene 1i was also reactive to undergo the E-I reaction to give product 2i in high yield (entry 8). When a trisubstituted alkene 1k was used, quaternary aldehyde 2k was obtained in 68% yield, presumably via alkyl migration in the isomerization step (entry 10).

With the success in selective oxidation of styrenes to arylacetaldehydes catalyzed by [Fe(2,6-Cl<sub>2</sub>TPP)CF<sub>3</sub>SO<sub>3</sub>], we extended this protocol to aliphatic alkenes which are problematic substrates in the ruthenium porphyrin-catalyzed E–I reaction and Pd-catalysed Wacker oxidation. When dodec-1-ene **3a** was treated with excess PhIO in the presence of 2 mol% [Fe(2,6-Cl<sub>2</sub>TPP) CF<sub>3</sub>SO<sub>3</sub>] in DCM at room temperature, only an epoxidation product was obtained in 74% yield without aldehyde being observed. Increasing temperature to 80 °C was found to effect the E–I reaction of **3a** to give aldehyde **4a** in 40% yield. The product yield was further improved to 70% using a stepwise procedure in the DCE/dioxane system, details of which are given in the ESI.†

With the optimized conditions, various aliphatic alkenes were examined. Most aliphatic alkenes underwent the Fe-catalyzed E–I reaction to give aldehydes in good yields (Table 3). In this work, the aliphatic alkenes used did not bear heteroatoms which are known to chelate with the palladium ion, thereby facilitating the Wacker oxidation of terminal alkenes to aldehydes. In the literature, this kind of aliphatic alkenes usually give methyl ketones as the main products under Wacker oxidation conditions.<sup>5b,5e,9</sup>

A tentative mechanism is proposed as depicted in Scheme 1. Iron(III) porphyrin catalyzes oxidation of alkene to epoxide. Subsequent activation of epoxide by the iron(III) porphyrin

 $\label{eq:Table 2} Table 2 \ The \ [Fe(2,6-Cl_2TPP)OTf] \ catalyzed \ E-I \ reaction \ of \ aryla alkenes to \ arylacetaldehydes$ 

[Fe(2,6-Cl <sub>2</sub> TPP)OTf] (2 mol%)					
	к × ——— 1	PhIO, DCM, RT 2	СНО		
Entry <sup>a</sup>	Alkene	Product	Yield <sup>b</sup> (%)		
1	Me 1b	ме СНО 2b	93		
2	MeO 1c	мео СНО 2с	64		
3	CI 1d	сі 2d	87		
4		CICHO2e	93		
5		CHO CI 2f	94		
6	F 1g	F 2g	86		
7	Br 1h	Br CHO 2h	92		
8		СНО 2і	85		
9	lj	2ј	57		
10		Ph CHO 2k	68		
	1k				

<sup>*a*</sup> 0.2 mmol PhIO; 0.6 mmol alkene; 2 mL DCM, rt, 6 h. <sup>*b*</sup> Yield based on <sup>1</sup>H NMR with PhTMS as the internal standard.

catalyst results in isomerization giving aldehyde as the final product. In this work, epoxide was observed in the course of the catalysis. When compared to the previous work on the ruthenium porphyrin catalyzed E–I reaction,<sup>6</sup> the cationic iron(III) porphyrin with the weakly ligating  $CF_3SO_3^-$  ligand is a strong Lewis acid, and this is needed to promote the E–I reaction of aliphatic alkenes.

α,β-Unsaturated esters are versatile compounds with many applications in organic synthesis.<sup>10</sup> As both E–I reaction and olefination of aldehyde<sup>11</sup> could be catalysed by iron(III) porphyrin, a one pot protocol to synthesize α,β-unsaturated esters from alkenes was developed. As shown in Scheme 2, when styrene was treated with PhIO in the presence of [Fe(2,6-Cl<sub>2</sub>TPP) CF<sub>3</sub>SO<sub>3</sub>] at room temperature for 4 hours, followed by reaction with EDA and Ph<sub>3</sub>P, α,β-unsaturated ester **5** was obtained in 84% isolated yield (Scheme 2, eqn 1). This iron catalysis could be easily modified to give 1,2-diols which are useful compounds in organic synthesis.<sup>12</sup> Treatment of styrene





 $^{a}$  0.2 mmol alkene; 0.22 mmol PhIO.  $^{b}$  Yield based on  $^{1}$ H NMR with PhTMS as the internal standard.





with PhIO and HCO<sub>2</sub>H in the presence of [Fe(2,6-Cl<sub>2</sub>TPP) CF<sub>3</sub>SO<sub>3</sub>] at room temperature for 10 hours and subsequent reaction with  $K_2CO_3$  and MeOH gave 1-phenylethane-1,2-diol in 73% yield (Scheme 2, eqn 2).

In conclusion, we have developed an efficient and selective 'Wacker-type' oxidation of terminal aryl- and aliphatic alkenes to aldehydes in high yields catalyzed by cationic iron(III) porphyrins with triflate as the counter anion. A one pot method for the synthesis of  $\alpha,\beta$ -unsaturated esters from alkenes has also been developed by combining the iron porphyrin catalyzed E–I reaction and olefination of aldehyde. By ring-opening of the epoxide intermediate, a dihydroxylation of alkenes was achieved.

We are thankful for the financial support of Hong Kong Research Grant Council (HKU 7052/07P, CityU 2/06C and HKU1/CRF/08), CAS-GJHZ200816 and CAS-Croucher Funding Scheme for Joint Laboratory, and the Areas of Excellence Scheme established under the University Grants Committee of the Hong Kong SAR, China (AoE/P-10/01). G.-Q. Chen thanks the Croucher Foundation of Hong Kong for the postgraduate studentship.

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