Efficient and Mild Oxidative Decarboxylation of Aryl-substituted Carboxylic Acids by Iron and Manganese Porphyrin Periodate Systems†

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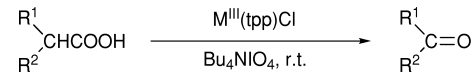
The oxidative decarboxylation of α-aryl carboxylic acids to the corresponding carbonyl derivatives was observed in catalytic systems containing tetrabutylammonium periodate and metallotetraphenylporphyrins (metal = Fe^{III} or Mn^{III}) at room temperature.

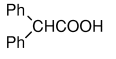
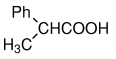
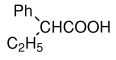
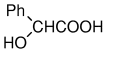
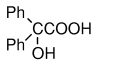
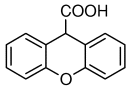
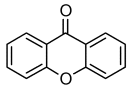
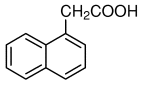
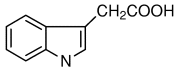
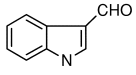
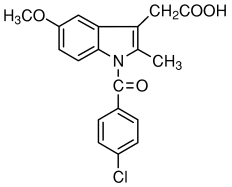
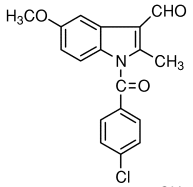
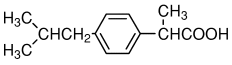
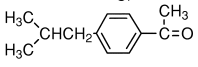
There has been considerable growth in understanding the catalytic action of metalloporphyrins in the last twenty years.[1,2] Numerous studies have been carried out employing metalloporphyrins in association with various single oxygen donors for the catalytic oxidation of alkenes,[3] alkanes,[4] amines,[5] phenols,[6] thiols[7] and sulfides.[8] Such investigations have resulted in a better understanding of oxidative metabolism of foreign organic compounds in biological systems by cytochrome P-450 and peroxidase. However, so far very few chemical model systems based on metalloporphyrin derivatives that catalyze the oxidative decarboxylation of carboxylic acids have been reported.[9,10]

In this report we wish to describe an efficient decarboxylation reaction using iron(III) and manganese(III) tetraphenylporphyrins as catalysts, M(tpp)Cl (0.012 mmol), for decarboxylation of α-substituted acetic acids, R^1R^2-CHCOOH (1 mmol), which afford the corresponding carbonyl derivatives in the presence of tetrabutylammonium periodate, Bu_4NIO_4 (2 mmol), in dichloromethane solution [reaction (1)].



(1)

Table 1 Oxidative decarboxylation of α-aryl carboxylic acids by $M^{III}(tpp)Cl/Bu_4NIO_4$[a]

Run	Substrate	Product	Yield[b] (%) (*t*/h)	
			$Fe^{III}(tpp)Cl/IO_4^-$	$Mn^{III}(tpp)Cl/IO_4^-$
1	$PhCH_2COOH$	PhCHO	88 (3)	84 (3)
2			94 (3)	90 (3)
3			92 (3)	87 (3)
4			93 (3)	90 (3)
5		PhCHO	95 (1)	92 (1)
6			94 (1)	92 (1)
7			93 (8)	89 (8)
8			74 (4)	70 (4)
9			60 (8)	57 (8)
10			71 (8)	61 (8)
11			94 (4)	90 (4)

[a]Reaction conditions: substrate (1 mmol), Bu_4NIO_4 (2 mmol), $M^{III}(tpp)Cl$ (0.012 mmol), CH_2Cl_2 (10 ml), room temperature. [b]Isolated yields.

The results which are summarized in Table 1 show that this catalytic system led to decarboxylation of aryl-substituted acetic acids to carbonyl derivatives in good isolated yields (57–95%) at room temperature. It was found

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that the principal product in all of the reactions was the carbonyl derivative and only a small amount of the alcohol derivative was observed. Here, we show that M^{III}(tpp)Cl can catalyze the selective oxidation by Bu_4NIO_4 of alcohols to carbonyl compounds. Iron(III) tetraphenylporphyrin exhibits a greater catalytic power than the corresponding manganese(III) compound, whereas the reverse situation was observed for epoxidation of alkenes.[11]

Decarboxylation of α-hydroxy carboxylic acids (Runs 5 and 6) were fast and completed in 1 h. By analogy with earlier studies,[9,10,12] the faster reaction rates can be assigned to the formation of relatively stable α-hydroxy alkyl radicals from interaction of the carboxylic acids with a highly electrophilic intermediate generated by IO_4^-–M^{III} porphyrin.

The oxidation of anti-inflammatory drugs such as Indomethacin and Ibuprofen (Runs 10 and 11) afforded corresponding carbonyl derivatives as the major products in 61 and 94% yields, respectively. Such an oxidative decarboxylation pathway has been also observed during metabolism of non-steroidal anti-inflammatory drugs.[10] In this report we have shown that these reactions can be efficiently mimicked using simple iron and manganese porphyrin.

Blank experiments, carried out on the α-aryl carboxylic compounds, showed that in the absence of catalyst, Bu_4NIO_4 has poor ability to decarboxylate aryl carboxylic acids at room temperature (5–10% yields). However, a literature search[13] showed that Bu_4NIO_4 in refluxing dioxane was able to convert aryl acetic acids into the corresponding carbonyl derivatives in yields between 50–85% only at long times (8–48 h).

Experimental

All chemicals used were reagent grade. The porphyrin ligand, tpp, was prepared and metalated according to the literature procedures.[14,15]

General Procedure for Oxidative Decarboxylation of α-Aryl Substituted Carboxylic Acids.—To a solution of the α-aryl carboxylic acids (1 mmol) in CH_2Cl_2 (10 ml), M^{III}(tpp)Cl (0.012 mmol) and Bu_4NIO_4 (2 mmol) were added and the solution stirred magnetically at room temperature for 1–8 h. Reaction progress was followed by TLC. Purification of crude products on a silica gel plate or silica gel column (eluent: CCl_4–Et_2O) afforded pure products in 57–95% yields (Table 1).

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