

# Practical dihydroxylation and C–C cleavage of unsaturated fatty acids

Michael A. Oakley<sup>a</sup>, Simon Woodward<sup>a,\*</sup>, Keith Coupland<sup>b</sup>, David Parker<sup>b</sup>,  
Clare Temple-Heald<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Hull, Kingston-upon-Hull HU6 7RX, UK

<sup>b</sup> Croda Universal, Oak Road, Clough Road, Kingston-upon-Hull HU6 7PH, UK

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## Abstract

Unsaturated fatty acids  $[\text{C}_8\text{H}_{17}\text{CH}=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{H}]$  ( $n = 7, 11$ ) acids are cleanly dihydroxylated by hydrogen peroxide in the presence of catalytic amounts of  $\text{H}_2\text{WO}_4$ . Under molecular oxygen, in the presence of catalytic amounts of *N*-hydroxyphthalimide and  $\text{Co}(\text{acac})_3$ , the diols resulting from erucic ( $n = 11$ ) and oleic ( $n = 7$ ) acid undergo C–C cleavage. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Dihydroxylation; C–C cleavage; Unsaturated fatty acids

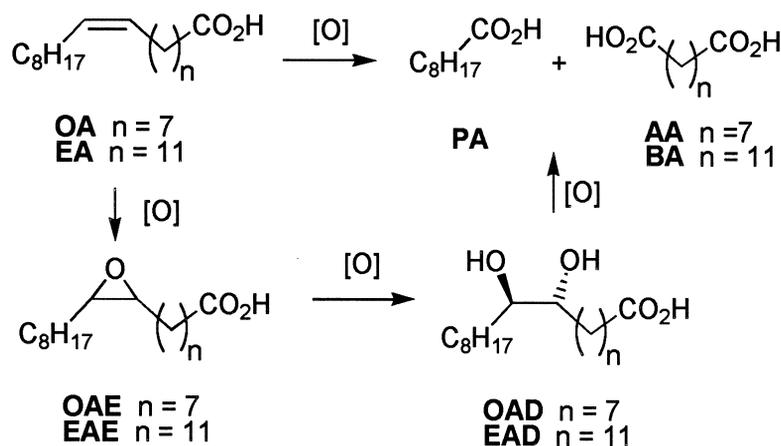
## 1. Introduction

Monounsaturated carboxylic acids are attractive starting materials in oleochemistry due to their ready availability from natural sources. Presently the large scale C=C transformation of this class of molecules is limited to epoxidation and some C–C cleavage reactions using ozone (for review, see Ref. [1]). Due to the technical difficulties associated with large scale ozonolysis, there is considerable interest in new C–C cleavage processes using alternative oxidants,

especially  $\text{H}_2\text{O}_2$  and molecular oxygen. The cleavage reactions of oleic (*cis*-9-octadecenoic) **OA** and erucic (*cis*-13-docosenoic) **EA** acids (Scheme 1) are typical and lead to pelargonic (nonanoic) acid **PA** and either azelaic (nonanedioic) **AA** or brassylic (tridecanedioic) acid **BA**. The derived epoxides (**OAE**, **EAE**) and diols (**OAD**, **EAD**) are often intermediates in non-ozone C=C cleavage reactions.

We sought a selective, metal catalysed, C–C cleavage reaction of **OA** and **EA** using only  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  (preferably just the latter) at atmospheric pressure and moderate temperature, and applicable to large scale use. These exacting conditions exclude nearly all known routes. For example, although alkenes readily cleave to carboxylic acids with  $\text{H}_2\text{O}_2$ , in the presence of

\* Corresponding author. Tel.: +44-1482-466549 (direct), +44-1482-465432 (laboratory); Fax: +44-1482-466410/470225; E-mail: s.c.woodward@chem.hull.ac.uk



Scheme 1.

polyoxometalates or other Group 6 derived catalysts, an excess of oxidant (typically 3–6 equivalents) is required [2–5]. The use of excess  $\text{H}_2\text{O}_2$  on large scales is problematic due to safety considerations and the sheer volume of the aqueous reagents required for low concentration aqueous  $\text{H}_2\text{O}_2$ . These difficulties can be overcome by using just one equivalent of  $\text{H}_2\text{O}_2$  to prepare epoxides (**OAE**, **EAE**). Unless special reaction conditions are employed [6–8] these undergo ring-opening to give the diols **OAD**, **EAD** [9]. Such diols may be cleaved with  $\text{H}_2\text{O}_2$  [3,4,10], or by using molecular oxygen. The aerobic C–C cleavages require the presence of cobalt(II) carboxylates [11,12] or various compounds of  $\text{Mo}^{\text{VI}}$  or  $\text{W}^{\text{VI}}$  (including polyoxometalates) in the presence of cobalt(II) salts [13–15]. These preparations typically involve the isolation of the diol as the presence of water, derived from  $\text{H}_2\text{O}_{2(\text{aq})}$ , is very deleterious to the subsequent autooxidation of the diol [11]. Although this can be overcome by the use of high-pressure reactions [14,15] or special solvents [11–13], in general, simple two step one-pot procedures for  $\text{H}_2\text{O}_2/\text{O}_2$  cleavage of alkenes at atmospheric pressures have not been realised. In this regard we were attracted by a recent claim that erucic acid could be cleaved using a  $\text{H}_2\text{WO}_4$  system alone and  $\text{H}_2\text{O}_{2(\text{aq})}/\text{O}_2$  as the oxidant

[16]. This formed the starting point for our investigation.

## 2. Experimental

### 2.1. General

Proton and  $^{13}\text{C}$  NMR spectra were recorded on either a Jeol JNM-GX270 or JNM-LA400 spectrometers using tetramethylsilane as standard;  $J$  values are given in Hz. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Mass spectra were obtained on a Finnigan-MAT 1020 (electron impact ionisation, EI). GC analyses were carried out on a Perkin Elmer 8320 instrument using a BP-1 column for methyl esters of the diols and epoxides, and a Sigma 3B instrument using a BP-20 column for methyl esters of the other acids. Typically the following conditions were used: head pressure = 12 p.s.i., injection port temperature =  $200^\circ\text{C}$ , oven programme =  $50^\circ\text{C}$  ramped to  $250^\circ\text{C}$  at  $30^\circ\text{C min}^{-1}$  (BP-20) or  $120^\circ\text{C}$  for 1 min, then ramped to  $320^\circ\text{C}$  at  $7^\circ\text{C min}^{-1}$  (BP-1), detector temperature =  $250^\circ\text{C}$ . Oxygen was presaturated with solvent vapour before bubbling into reaction mixtures to minimise solvent evaporation.

## 2.2. 13,14-Epoxyerucic acid methyl ester

A sample of genuine 13,14-epoxyerucic acid methyl ester **EAEMe** was prepared by treatment of neat erucic acid **EA** (1.76 g, 5.00 mmol) with anhydrous TBHP (6.00 mmol, 3 M in isooctane or 5 M in nonane) in the presence of 0.5 mol% Mo(CO)<sub>6</sub>. The reaction was heated to 100°C for 3 h and the epoxide isolated by removal of the volatiles under vacuum followed by extraction into CH<sub>2</sub>Cl<sub>2</sub> to yield a colourless solid, 1.75 g, 95%. <sup>1</sup>H NMR (270 MHz, CD<sub>3</sub>OD) d<sub>H</sub> 0.90 (3 H, t, *J* 7.2, –Me), 1.20–1.65 (34 H, m, 17 × CH<sub>2</sub>), 2.25 (2 H, t, *J* 7.4, –CH<sub>2</sub>CO<sub>2</sub>–), 3.36 (2 H, m, –HC(O)CH–).

## 2.3. General procedure for H<sub>2</sub>WO<sub>4</sub>-catalysed oxidation of erucic acid EA

A glass reactor vessel with an internal construction designed to facilitate the dissolution of bubbled O<sub>2</sub> into the solvent, fitted with a gas inlet, a condenser and an efficient mechanical stirrer was charged with erucic acid **EA** (27.0 g, 80.0 mmol), H<sub>2</sub>WO<sub>4</sub> (2.00 g, 8.00 mmol; 10 mol%) and *tert*-butyl alcohol (TBA, 160 cm<sup>3</sup>). H<sub>2</sub>O<sub>2</sub> (9.0 cm<sup>3</sup>, 80 mmol; 30% solution) was added slowly with stirring and the reactor vessel heated to 75°C. (**Caution!** Above 75°C the TBA/O<sub>2</sub> vapours above the reaction can enter an explosive regime.) O<sub>2</sub> was introduced at a rate of ca. 2 cm<sup>3</sup> s<sup>-1</sup> and stirring continued for 4 days. The mixture was filtered while hot and allowed to cool. After 24 h, 13,14-dihydroxydocosanoic acid (colourless solid, 11.0 g, 37%) was filtered off [<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) d<sub>H</sub> 0.89 (3 H, t, *J* 6.8, –Me), 1.25–1.38 (28 H, m, 14 × CH<sub>2</sub>), 1.38–1.55 (4 H, m, 2 × –CH<sub>2</sub>CHOH–), 1.59 (2 H, quintet, *J* 7.1, –CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>–), 2.26 (2 H, t, *J* 7.4, –CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>–), 3.32 (2 H, m, 2 × –CHOH–)]. The solvent was removed from the mother liquors and lauric acid (17.24 g, 80.0 mmol, GC IS) and MeOH (200 cm<sup>3</sup> of a 1 wt.% H<sub>2</sub>SO<sub>4</sub> solution) added. The mixture was heated to reflux for 30 min and subjected to GC analysis.

(Conditions: SGE BP20 capillary column 25 m, i.d. 0.25 mm, He carrier gas, H<sub>2</sub> FID, program: initial temp. 50°C, ramp 30°C min<sup>-1</sup> to 250°C).

## 2.4. Oxidative cleavage of 13,14-dihydroxydocosanoic acid EAD by *N*-hydroxyphthalimide (NHPI)

To a 25-cm<sup>3</sup> round bottomed flask equipped with a magnetic stirrer, a condenser and an O<sub>2</sub> inlet at the base was added **EAD** (750 mg, 2.0 mmol), NHPI (8 mg, 0.05 mmol, 2 1/2 mol%) and Co(acac)<sub>3</sub> (8 mg, 0.02 mmol, 1 mol%) were added, and the flask was placed in a bath preheated to 75°C. O<sub>2</sub> was introduced at a rate of 0.5 cm<sup>3</sup> min<sup>-1</sup> and stirring continued for 3–5 h. The hot mixture was transferred into a 50 cm<sup>3</sup> flask containing lauric acid (400 mg, 2.0 mmol; GC IS) and 1 wt.% H<sub>2</sub>SO<sub>4</sub> in MeOH (30 cm<sup>3</sup>) added. The solution was heated to reflux for 1 h and analysed by GC as above.

## 2.5. General procedure for the oxidation of EA by H<sub>2</sub>WO<sub>4</sub>/Co(acac)<sub>3</sub>/NHPI

To a 25-cm<sup>3</sup> round bottomed flask equipped with a magnetic stirrer, a condenser and an O<sub>2</sub> inlet at the base was added **EA** (644 mg, 2.0 mmol), H<sub>2</sub>WO<sub>4</sub> (8 mg, 0.03 mmol; 1 mol%) and TBA (5 cm<sup>3</sup>). H<sub>2</sub>O<sub>2</sub> (218 μL, 11 M; 1.2 equiv.) was added dropwise with stirring and the mixture was heated to strong reflux for 2 h. The heating bath was removed and replaced with a bath preheated to 75°C, NHPI (8 mg, 0.05 mmol, 2 1/2 mol%) and Co(acac)<sub>3</sub> (8 mg, 0.02 mmol, 1 mol%) were added, O<sub>2</sub> introduced at a rate of 0.5 cm<sup>3</sup> min<sup>-1</sup> and stirring continued for 3–5 h.

### 2.5.1. Yield determination by GC

The hot mixture was transferred into a 50 cm<sup>3</sup> flask containing lauric acid (400 mg, 2.0 mmol; GC IS) and 1 wt.% H<sub>2</sub>SO<sub>4</sub> in MeOH (30 cm<sup>3</sup>) added. The solution was heated to reflux for 1 h and analysed by GC as above.

### 2.5.2. Representative product isolation

A oxidised **EA** mixture, which assayed by GC as containing 54% cleavage products (**PA**, **BA**), was allowed to cool and filtered to remove catalyst and precipitated diol. The solvent was removed, the residue dissolved in Et<sub>2</sub>O and stirred for 1 h with dil. HCl. The organic phase was separated, washed with brine, dried MgSO<sub>4</sub>, and the solvent removed. **NA** was removed by distillation (Kugelrohr, 0.1 mm, 100°C; colourless oil, 136 mg, 43%) and **BA** crystallised from MeOH to yield a colourless solid, 230 mg, 48%.

## 3. Results and discussion

Aerobic C–C cleavage of **EA** in the presence of H<sub>2</sub>WO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> in wet *tert*-butyl alcohol (TBA) [16] led, in our hands, to a mixture of products. Typically, 13,14-dihydroxydocosanoic acid **EAD** (37%) could be isolated from the reaction mixture after 72 h. Alternatively, following addition of lauric acid as internal standard and methyl ester derivatisation by 1% H<sub>2</sub>SO<sub>4</sub> in MeOH, GC yields of between 40% and 49% **BA** and **PA** could be obtained, together with up to 6% unreacted **EA**, indicating a mass balance of ca 92%. The course of the H<sub>2</sub>WO<sub>4</sub>-catalysed reaction between erucic acid **EA** and 30% hydrogen peroxide under molecular oxygen was monitored by GC. After 24 h reaction time, only a trace of **EA** remains in the reaction mixture, along with ca 2% cleavage products. The cleavage products then begin to appear, reaching a maximum after 3 days. No **EAE** is apparent in the reaction mixture by comparison with authentic material indicating that conversion to the diol **EAD** is rapid under the reaction conditions. These studies confirmed that aerobic autoxidation of such diols is slow in the presence of oxo species derived from H<sub>2</sub>WO<sub>4</sub> and this leads us to look for additional promoters for this part of the transformation. Such promoters must be able to operate under the protic, partially aqueous, conditions created by the use of H<sub>2</sub>O<sub>2(aq.)</sub> [11].

Recently, Iwahama et al. [17] reported the oxidation of 1,2-diols to diones in good yield by molecular oxygen catalysed by 10 mol% *N*-hydroxyphthalimide (NHPI) and 2 mol% Co(acac)<sub>3</sub> in acetonitrile. Significant C–C cleavage, resulting in carboxylic acids, can occur in this chemistry. A more active NHPI system, using catalytic Mn(acac)<sub>3</sub> in AcOH at 100°C, is effective in the oxidation of cyclohexane to adipic acid [18]. To identify optimal conditions for improving the C–C cleavage rate with in situ generated **EAD**, the isolated diol was first subjected to trial variation in metal promoter and solvent in the presence of 10 mol% NHPI (Table 1).

While the standard Ishii diol oxidation conditions [17] provided only modest yields of cleaved products (run 1), this was considerably improved by appropriate condition choice. Acetic acid proved to be a better solvent than acetonitrile (runs 2–5) with similar reactivity attained with both cobalt and manganese catalysts. Fortuitously, *tert*-butyl alcohol (TBA) is found to be the solvent of choice for the cleavage of **EAD**, with greater than 60% yield by GC with bubbling O<sub>2</sub> (Run 7). The effect of reducing the catalyst loading in the system NHPI/Co(acac)<sub>3</sub> in TBA at 75°C was then investigated, as shown in Table 2. The reaction is capable of tolerating NHPI loadings from 10 to 2 1/2 mol% (2 1/2 mol% NHPI represents a 1 wt.% loading with respect to diol **EAD**) (Runs 1–3). Lowering the Co loading has greatly reduces the cleavage

Table 1  
Oxidative cleavage of **EAD** under NHPI/M(acac)<sub>3</sub> catalysis

Run	Solvent	T (°C)	M	O <sub>2</sub>	Yield (%)	
					BA	NA
1	MeCN	75	Co	S	41	35
2	AcOH	75	Co	S	53	73
3	AcOH	100	Co	S	46	56
4	AcOH	100	Mn	S	50	67
5	AcOH	100	Mn	B	33	38
6	TBA	75	Co	S	57	53
7	TBA	75	Co	B	62	69

Conditions: **EAD** (2.00 mmol), M(acac)<sub>3</sub> (0.04 mmol), and NHPI (0.20 mmol) heated in the solvent (12 cm<sup>3</sup>) under either a static (S) O<sub>2</sub> atmosphere or with O<sub>2</sub> bubbling (B) for 16 h.

Table 2  
Optimisation of **EAD** cleavage using NHPI/Co(acac)<sub>3</sub>

Run	NHPI (mol%)	Co (mol%)	t (h)	O <sub>2</sub>	Yield (%)	
					BA	NA
1	10	2	24	S	57	51
2	5	2	24	S	62	61
3	2 1/2	2	24	S	53	60
4	10	1/2	24	S	27	26
5	2 1/2	1	1	S	trace	trace
6	2 1/2	1	1	B	trace	trace
7	2 1/2	1	5	S	trace	trace
8	2 1/2	1	5	B	72	67
9	2 1/2	1	24	S	trace	trace
10	2 1/2	1	24	B	74	61

Conditions: **EAD** (2.00 mmol), Co(acac)<sub>3</sub> (0.04–0.01 mmol), and NHPI (0.20–0.05 mmol) were heated in TBA (12 cm<sup>3</sup>) under either a static (S) O<sub>2</sub> atmosphere or with O<sub>2</sub> bubbling (B).

yields attained under static oxygen atmospheres (run 4). However, with catalyst loadings of 2 1/2 mol% NHPI and 1 mol% [Co] (equivalent to ca 1 wt.% of each) and O<sub>2</sub> bubbling gives complete conversion and good yields of cleaved products in 5 h (runs 5–10).

Having established that the Co(acac)<sub>3</sub>/NHPH system works well for cleavage of isolated **EAD** the catalyst systems was tested on in situ material prepared from **EA** by H<sub>2</sub>WO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> oxidation. The results of several runs in order to minimise the catalyst quantities are shown in Table 3. Initially the procedure was run with 10 mol% H<sub>2</sub>WO<sub>4</sub> (identical to that used in the original tungsten aerobic C–C cleavage [16]) with the NHPI and cobalt loading as described by Iwaham et al. [17] (runs 1–2). This initial procedure is an improvement over catalysis by H<sub>2</sub>WO<sub>4</sub> alone. However, as most of the C–C cleavage is now being carried out by Co/NHPI catalysis of the H<sub>2</sub>O<sub>2</sub> **EA**, oxidation/hydrolysis can be accomplished with a much lower tungsten loading and in a significantly shorter time. Complete conversion of **EA** is accomplished within 2 h at a H<sub>2</sub>WO<sub>4</sub> loading of 1 1/2 mol%. The effect of lowering the NHPI loading was determined (runs 3–5), coupled with the further reduction in W<sup>VI</sup> catalyst concentration. These reactions show that not only does the cleavage

tolerate the reduction of the NHPI loading to as low as 1/2 mol%, but that yields are actually improved as NHPI concentration is reduced. Decreasing the Co loading, at 2 1/2 mol% phthalimide, shows only a slight decrease in observed cleavage products at 1/4 mol% (runs 6–7). Run 8 shows that good yields of cleaved products are still obtained in 5 h at catalyst loadings of 1/2 mol% NHPI and 1/4 mol% Co. This represents catalyst turnovers, per C–OH bond oxidised, of 400 and 800, respectively. However, the presence of Co is still required for good yields, with only ca. 13% yield in the complete absence of Co(acac)<sub>3</sub> (run 9).

Finally, the oxidative cleavage of oleic acid, methyl erucate, methyl oleate and linoleic acid was performed. These results are shown in Table 4. Comparable degrees of C–C cleavage are attained with both **EA** and its methyl ester but surprisingly oleic acid **OA**, and its methyl ester, do not perform as well (runs 1–3). As erucic acid **EA** is cleaved with high efficiency, we suspected the radical oxidation chain to be carried particularly effectively by an intermediate derived from **EA** or **EAD**. Supporting this idea, when a mixture of 1 mmol **EA** and 1 mmol **OA**

Table 3  
Complete oxidation of **EA** by combined H<sub>2</sub>WO<sub>4</sub>/Co(acac)<sub>3</sub>/NHPH catalysis

Run	W (mol%)	T (h)	NHPI (mol%)	Co (mol%)	T (h)	O <sub>2</sub>	Yield	
							BA	NA
1	10	24	10	2	24	S	59	56
2	10	24	10	2	24	B	51	50
3	1 1/2	2	2 1/2	1	3	B	58	56
4	1 1/2	2	1 1/4	1	3	B	63	71
5	1 1/2	2	1/2	1	3	B	64	64
6	1 1/2	2	2 1/2	1/2	3	B	54	54
7	1 1/2	2	2 1/2	1/4	3	B	50	41
8	1 1/2	2	1/2	1/4	5	B	61	54
9	1 1/2	2	2 1/2	0	3	B	14	13

Conditions: **EA** (2.00 mmol) and H<sub>2</sub>WO<sub>4</sub> (0.20 or 0.03 mmol) treated with H<sub>2</sub>O<sub>2</sub> (2.40 mmol) in TBA (4 cm<sup>3</sup>) for 2 or 24 h. After addition of Co(acac)<sub>3</sub> (0–0.04 mmol), and NHPI (0.01–0.20 mmol) the reaction was heated under either a static (S) O<sub>2</sub> atmosphere or with O<sub>2</sub> bubbling.

Table 4

Alkene cleavage by H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub> using combined H<sub>2</sub>WO<sub>4</sub>/Co(acac)<sub>3</sub>/NHPI catalysis

Run	Substrate(s)	W (mol%)	t (h)	NHPI (mol%)	Co (mol%)	t (h)	Yield (%)
1	Methyl erucate	1	2	2 1/2	1	3	<b>PA</b> 54 <b>BA</b> 41
2	<b>OA</b>	1	2	2 1/2	1	3	<b>PA</b> 15 <b>AA</b> 15
3	Methyl oleate	1	2	2 1/2	1	3	<b>PA</b> 20 <b>AA</b> 19
4	1:1 <b>EA:OA</b>	1	2	2 1/2	1	3	<b>PA</b> 56 <b>AA</b> 56 <b>BA</b> 56
5	Linoleic acid	1	2	2 1/2	1	3	< 10% conversion
6	Decene	10	24	10	2	24	<b>VA</b> 20
7	Tetradecene	10	24	10	2	24	<b>HA</b> 39

Conditions: The unsaturated acid (2.00 mmol) and H<sub>2</sub>WO<sub>4</sub> (0.20 or 0.02 mmol) treated with H<sub>2</sub>O<sub>2</sub> (1.2 equiv. per double bond) in TBA (4 cm<sup>3</sup>) for 2 or 24 h. After addition of Co(acac)<sub>3</sub> (0.02–0.04 mmol), and NHPI (0.05–0.20 mmol) the sample was heated in with O<sub>2</sub> bubbling.

**VA** = valeric acid; **HA** = heptanoic acid.

is oxidised yields of 0.56 mmol **BA**, 1.12 mmol **PA** and 0.56 mmol **AA** are attained (run 4). Such co-oxidation effects are not widely reported although we are aware of one patent claim [19].

Linoleic acid, C<sub>5</sub>H<sub>17</sub>(CH=CHCH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>-CO<sub>2</sub>H, proved essentially inert to oxidation on its own. A similar simultaneous oxidation performed on a 1:1 molar mixture of **EA** and linoleic acid leads to some conversion. In this instance **PA** and **BA** (from **EA**) are each obtained in 20% yield and caproic (hexanoic) acid **CA** and **AA** (from linoleic acid) were obtained in 30% and 27% yield, respectively. The central, doubly allylic methylene group of oleic acid should give, in the current reaction, malonic acid (HO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>H). Although a genuine sample of malonic acid is readily derivatised by acidified MeOH, no dimethyl malonate is observed in the GC analysis of the oxidation reaction products for linoleic acid. It is assumed that the malonate fragment undergoes further reaction in the oxidation conditions. Either the malonate derived products are responsible for inhibiting the reaction or the radical species generated from the central methylene fragment are unreactive in the aerobic C–C cleavage reaction.

When the standard H<sub>2</sub>WO<sub>4</sub>/Co(acac)<sub>3</sub>/NHPI conditions are applied to simple alkenes *trans*-dec-5-ene and *trans*-tetradec-7-ene most of the starting material was recovered unreacted. The

more vigorous conditions of Table 4 (runs 6–7) are required for complete reaction, and yields were considerably lower than for fatty acids. This observation indicates that the presence of a carboxyl group within the substrate is required for efficient catalysis with H<sub>2</sub>WO<sub>4</sub>. When the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>WO<sub>4</sub> dihydroxylation reaction is performed on *trans*-dec-5-ene in the presence of lauric acid no improvement over the reaction of the alkene alone is observed, indication that directing group effects are important.

In conclusion, a new approach to the two step one pot cleavage of monounsaturated fatty acids has been achieved. The use of *N*-hydroxyphthalimide derived radicals obtained from Co(acac)<sub>3</sub>/O<sub>2</sub> allows autoxidation of diols derived from aqueous H<sub>2</sub>O<sub>2</sub> in the presence of H<sub>2</sub>WO<sub>4</sub> without the reaction inhibition normally seen in these transformations [11].

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