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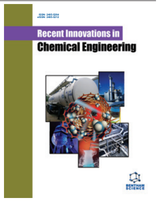
RESEARCH ARTICLE



Green Procedure for One-Pot Synthesis of Azelaic Acid Derivatives Using Metal Catalysis

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ARTICLE HISTORY

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Abstract: ***Background & Objective***: A green one-pot synthesis of oleic acid (**1**) derivatives is promoted by Rare Earth Metal (REM) triflates and commercial Molybdenum dioxo dichloride ($MoCl_2O_2$) in the presence hydrogen peroxide as a green oxidant.

Results: The protocol permits to govern the oxidation selectivity by simply choosing the proper combination of Mo and Sc catalysts.

Conclusion: Methyl oleate epoxide **2a** and azelaic acid **6** thus obtained are valuable industrial intermediates for synthesizing bio-compostable plastics, plasticizers of PVC, lubricating oils, cosmetics and pharmaceuticals (bactericides, anti-inflammatories, *etc*.).

Keywords: Removable resource, rare earth, molybdenum complex, sustainability, azelaic acid, green chemistry.

1. INTRODUCTION

In these years the green progress has grown compelling trend thanks to the research and manufacturing. While the search for alternative sources to petroleum to produce energy has been very developed even today, the problems related to the production of new materials and products able to adequately replace non-biodegradable plastics have not been adequately addressed [1].

A promising approach is to use biomass; in particular plants, trees, agriculture crops, and algae. Some valuable chemicals are easily produced from these renewable carbon resources, such as lipids and oleic acid (**1**) [2,3]. The latter is one of the most abundant unsaturated fatty acids in nature, which finds applications in foods and as an ingredient in soaps and detergents industry [2]. One of its main oxidation products, namely azelaic acid **6**, is a valuable industrial intermediate to produce fibers, pharmaceuticals, cosmetics, plastics, and adhesives [3, 4]. Therefore, the search for new useful methods for converting oleic acid into azelaic acid **6** is considered mandatory.

The oxidation steps of **1** for the transformation of oleic acid include: i) epoxidation, ii) epoxide ring opening to give 1,2 diols, and iii) C=C double bond cleavage (Chart **1**).

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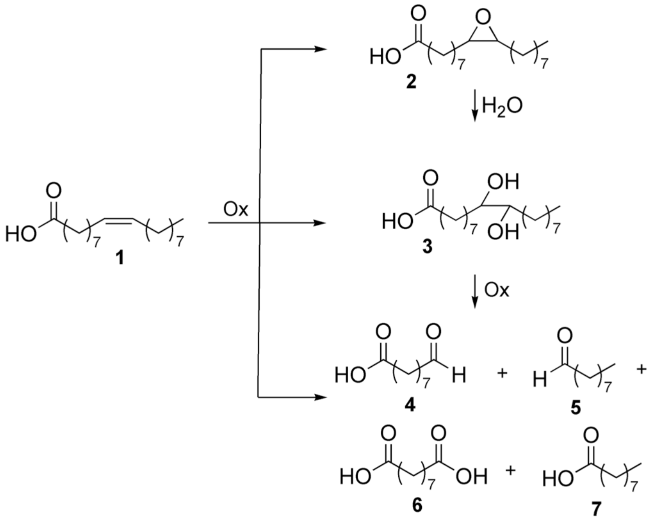


Chart (1). Oxidation ways.

In principle, the desired azelaic acid **6** (together with by-product pelargonic acid **7**) can be generated through the direct double bond cleavage process, as well as by the tandem multistep procedures involving epoxide **2** and 1,2-diol **3** as the intermediates [4-8]. Generally, vegetable oils can be epoxidized with performic acid, which is generated *in situ* (for safety reasons) by reacting HCOOH with hydrogen peroxide in the presence of various inorganic Bronsted acids as catalysts (commonly HBF_4 or H_3PO_4) [9].

Recently, Molybdenum and some rare earth derivatives (Sc and Yb), by their Lewis acid properties, displayed interesting activity in the oxidation of olefins [10-12], therefore, we planned their involvement in the oxidation of oleic acid **1** and corresponding methyl ester **1a**, to replace the non-eco-friendly and unrecyclable HBF_4 and H_3PO_4.

In addition, being much safer, [13] Mo can be considered a green alternative to the typical heavy metals in the petroleum and plastic industries. In particular, molybdenum(VI) dichloride dioxide ($MoCl_2O_2$) and its related complexes, serve well as Lewis acid catalysts for several transformations [14], ranging from oxidation to acylation, reduction, carbamylation, [15, 16] and methanolysis of vegetal oils [9].

Following our ongoing efforts in the field of oxidation, with the aim of producing valuable fine chemicals and industrial intermediates from renewable sources [17-21], we developed a flexible protocol for converting methyl oleate (**1a**) into its epoxide **2a** or azelaic acid **6**, by governing the selectivity of oxidation with H_2O_2 as green oxidant because its reduction product is only H_2O, in accordance with the Rules of green chemistry [22], and with a suitable combination of $MoCl_2O_2$ and $Sc(OTf)_3$ as catalysts [1, 23].

2. MATERIALS AND METHOD

NMR spectra were recorded on an Agilent Technologies 500 and 300 MHz Bruker spectrometer; the ^1H resonance signals were referenced to residual isotopic impurity of $CDCl_3$ (7.26 ppm). GC/MS experiments were run on a Shimadzu GLC 17-A instrument connected with a Shimadzu QP5050A selective mass detector using an SLB-5MS column (30 m × 0.25 mm id, film thickness 0.25 μm). Mass spectra were performed in EI mode (70 eV). FTIR spectra are recorded on Perkin Elmer instrument and are relative to KBr pellets or films (deposited on KBr plates).

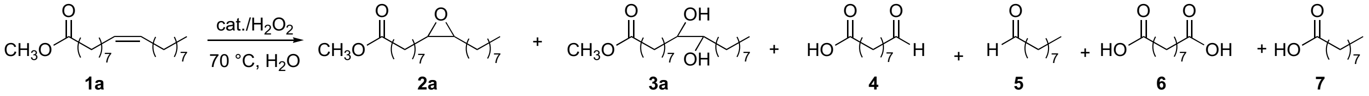
Solvents were purified by standard methods. All reagents were purchased in the highest purity available from scientific chemicals suppliers and used without purification.

3. EXPERIMENTAL

3.1. General Procedure for Oxidation of Methyl Oleate (1a) with H_2O_2 in Water Solution

To a stirred solution of HCOOH 85% (19.2 μL, $4.22 \cdot 10^{-4}$ mol), H_2O_2 50% (188 μL, 33.08 10^{-4} mol), and catalyst (14.7 10^{-6} mol, 3.6 mol% of namely $MoCl_2O_2$, $Sc(OTf)_3$, $Yb(OTf)_3$, or $La(OTf)_3 \cdot H_2O$ amounting at 2.92, 7.23, 9.12, and 8.87 mg, respectively) methyl oleate (**1a**) (140 μL, $4.12 \cdot 10^{-4}$ mol) was added. Then, the solution was heated at 70°C and left to react for the appropriate reaction time. The progress of the reaction was monitored by GC-MS set in scan mode. After completion of reaction, the mixture was diluted with distilled water and extracted with 2 mL of CH_2Cl_2 to remove catalysts. The organic phase was evaporated under vacuum and the residue was submitted to silylation procedure to evaluate both conversions and product ratio of Table **1**. In the case of reactions under conditions of entry 5, the aqueous phase was evaporated in vacuo to recover $Sc(OTf)_3$, which after drying was re-used at least five times.

Table 1. Epoxidation of Methyl oleate (1a) with H_2O_2 catalyzed by Rare earth triflates and Mo(VI)[a].



Entry	Catalyst	Co-catalyst	Time (h)	Conv. (%)	Product Ratio[b] (%)					
					2a	3a	4	5	6	7
1	$Sc(OTf)_3$	HCOOH	2	98	52	34	6	5	traces	
2	$Yb(OTf)_3$	HCOOH	2	93	48	34	5	7	traces	
3	$La(OTf)_3{\cdot}H_2O$	HCOOH	2	96	50	28	8	7	traces	
4	$Sc(OTf)_3$	HCOOH	8	98	48	37	8	6	traces	
5	$Sc(OTf)_3$	------------	8	97	60	40	-	-	-	
6	$MoCl_2O_2$	HCOOH	2	98	26	-	25	15	26	7
7	$MoCl_2O_2$	HCOOH	8	97	15	-	-	-	44	41
8	$MoCl_2O_2$	------------	2	99	82	-			3	15
9	$MoCl_2O_2$	------------	8	99	9	-	-	-	39	52
10	$MoCl_2O_2$[c]	$Sc(OTf)_3$[c]	2	98	78	20	-	-	-	-

[a]Reaction conditions: Methyl oleate 1a ($4.12{\cdot}10^{-4}$ mol), H_2O_2 50% ($33.08{\cdot}10^{-4}$ mol), catalyst ($14.7{\cdot}10^{-6}$ mol), HCOOH co-catalyst ($4.2{\cdot}10^{-4}$ mol) at 70 °C in water as the solvent. [b]Evaluated based on GLC peak area values after silylation reaction (see experimental section)± 2%. [c] $MoCl_2O_2$ 1 mol% ($1{\cdot}10^{-6}$ mol) and $Sc(OTf)_3$ 0.5 mol% ($0.5{\cdot}10^{-6}$).

3.2. Synthesis of Epoxide 2a on Grams Scale

To validate the epoxidation protocol, the reaction was repeated on grams scale. At this point, 0.500 g (0.169 mol) of methyl oleate **1a** was treated, in a 50 mL round-bottomed flask, with 0.77 mL of H_2O_2 50% (0.0356 mol) and 12mg of $MoCl_2O_2$ ($6.03\ 10^{-5}$ mol) under the same reaction condition previously reported. After 2 hours, the reaction mixture was transferred into a separating funnel and extracted with dichloromethane (3×20 mL). The combined organic phases were dried ($MgSO_4$) and the solvent was removed under vacuum affording epoxide **2a** in 78% yield (0.412 g) and 98% purity (GLC). Methyl oleate epoxide (**2a**): [9] ^{1}H-NMR ($CDCl_3$, 500 MHz) δ3.66 (s, 3H, C*H_3*); 2.91-2.87 (m, 2H, C*H*Oepox), 2,31-2.28 (t, 2H, *J* 8Hz, C*H_2*COO) 1. 63-1.27 (m, 26H), 0.89-0.86 (t, 3H, *J* 6.5 Hz). FT-IR (neat on KBr plate): 2930, 2853, 1743,1695, 1452, 1200, 1170 cm^{-1}.

3.3. Synthesis and Separation of Azelaic Acid (6) and Pelargonic Acid (7) on Grams Scale

To validate the protocol, the reaction was repeated on grams scale. At this stage, 1 g of methyl oleate **1a** ($3.37\ 10^{-3}$ mol) was treated, in a 50 mL round-bottomed flask, with 1.54 mL of H_2O_2 50% ($27.11\ 10^{-3}$ mol) and 23.93 mg of $MoCl_2O_2$ (0.12 mmol) under the same reaction condition previously reported. After 8 hours, the resulting aqueous suspension was transferred into a separating funnel and extracted with ethyl acetate (3×20 mL). Pelargonic acid **7**, which passed into the organic phase, was isolated after the solvent evaporation under vacuum (0.269 g, $1.70\ 10^{-3}$ mol 45% of yield and 90% of purity). Azelaic acid **6**, which remained suspended in the aqueous phase, was filtered and washed with cold water to remove catalyst residue (0.278 g, $1.48\ 10^{-3}$ mol, 44% of isolated yield, purity > 95%). Both products **6** and **7** gave spectral data in agreement with the literature [24]. Azelaic acid (**6**): ^{1}H-NMR (D_2O 40°C, 300 MHz) δ8.5 (s, 1H, CO*O<u>H</u>*), 2.19 (t, 4H, *J* 9H, C*<u>H_2</u>*COOH) 1.59-1.57 (m, 4H, C*<u>H_2</u>*CH_2COOH), 1,34-1.28 (m, 6H). FTIR (KBr pellets) 3506 (st *OH* free), 3463 (st *OH*), 2929, 2852, 1738 (st. *C=O* free) 1616 st. *C=O*), 1440, 1431 cm^{-1}. Pelargonic acid (**7**): ^{1}H-NMR ($CDCl_3$, 300 MHz) δ2.32-2.27 (t, 2H, *J* 7.2 Hz, C*<u>H_2</u>*COOH), 1.60-1.59 (m, 4H), 1.31-1.25 (m, 8H), 0.89-0.85 (t, 3H, *J* 7.2, C*<u>H_3</u>*-). FT-IR (neat on KBr plate):3424 (st *OH*), 2951,2881,2851, 1708 (*CO*OH, 1635, 1432,1410, 1293 cm^{-1}.

3.4. General Procedure for Silylation

To obtain reproducible and resolved chromatographic peaks, reaction products were converted into the corresponding silylated compounds. In a typical derivatization procedure [25], a weighed amount of the reaction mixture (30 mg) was treated, in a 10 mL centrifuge tube, with excess amounts (200 mg ca.) of a mixture composed by hexamethyldisilazane/trimethylchlorosilane/pyridine in a 3/1/9 weight ratio, respectively. The tube was sealed, stirred for 5 min and incubated at room temperature for 30 min causing the precipitation of NH_4Cl as a white solid. After centrifugation at 2500 rpm for 5 min, the clear supernatant was analyzed by GC–MS to assess both conversions and products ratio reported in Table **1**. (see supporting information Figure **S7-S10**).

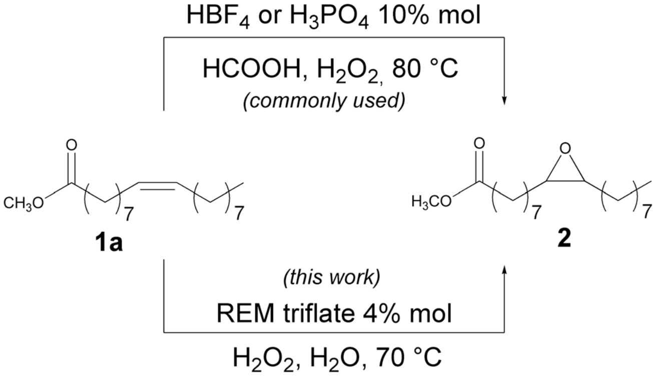
4. RESULTS AND DISCUSSION

Rare earth metal (REM) cations, especially their triflate salts, exhibit Hard Lewis acidity, stability in aqueous media and good affinity for oxidants [26]. Starting from the first example regarding catalytic ability of $Yb(OTf)_3$, many processes proved to be promoted by these metals in aqueous media [27]. More recently, Scandium(III) and Ytterbium(III) triflates have been used as co-catalysts of Mn complexes in the epoxidation of styrene [12]. To date, none of them have been employed in the oxidation of unsaturated fatty acids. With this in mind, we exploited the Lewis acids properties of these rare earth elements to replace the non-eco-friendly and unrecyclable HBF_4 or H_3PO_4 to improve the whole eco-sustainability of the oxidation process (Scheme **1**).

Indeed, REM triflates show the advantages of being green and easily removable from the reaction mixture and ready to be reused (see experimental section).

Oxidation conditions were surveyed on methyl oleate 1a as the substrate and reaction parameters were calibrated for processing 0.4 mmol of unsaturated fatty ester 1a, H_2O_2 50% ($33.08\ 10^{-4}$ mol), catalyst (3.6 mol%), co-catalyst (0.4 mmol), in water as the green solvent [1, 26]. Best temperature conditions were established to be 70°C, according to the literature [8, 9].

Initially, investigations were focused on the epoxidation process of methyl oleate 1a involving rare earth triflates $Sc(OTf)_3$, $Yb(OTf)_3$, and $La(OTf)_3{\cdot}H_2O$ as catalysts in the presence of HCOOH. As expected, formic acid played the role of oxygen carrier from H_2O_2 to the double bond through the formation of performic acid intermediate. Reactions occurred with complete conversion in relatively short times (2 h) but showed moderate selectivities towards epoxidation product 2a affording also appreciable amounts of 1,2-diol 3a and double bond cleavage by-products 4-7 (Table **1**, entries 1-3). Similar results were obtained by prolonging the reaction time up to 8 hours (Table **1**, entry 4).



Scheme (1). Epoxidation of Methyl oleate (1a).

Next, we decided to explore the catalytic properties of rare earths in the absence of formic acid. Results showed that selectivity improved using Scandium triflate alone, that led to the complete conversion of methyl oleate 1a into the epoxide 2a (60%) and 1,2-diol 3 (40%) without the formation of cleavage by-products (Table **1**, entry 5). This indicates that $Sc(OTf)_3$ possessing unique Lewis acid properties is capable of activating double bond for epoxidation, or electrophilically the hydrogen peroxide, even with longer reaction times [11, 12], but cannot give cleavage products.

Conversions and selectivities observed are even in agreement with those previously reported for epoxidation with Scandium triflate of cyclohexene [10] and styrene [12]. On these bases, we envisioned these rare earths, being green and recyclable, can be a potential alternative to HCOOH in activating the hydrogen peroxide, thus making the epoxidation of 1a suitable for a possible industrial application.

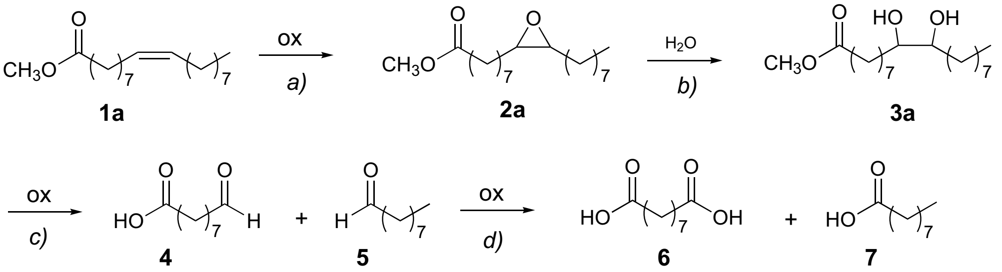
With the aim of achieving a complete control of selectivity, due to the also the practical importance of obtaining azelaic acid, we searched the conditions to get selectively the C=C bond cleavage products 6 and 7. Following our ongoing efforts in exploiting the catalytic properties of $MoCl_2O_2$, we evaluated its application to our process considering the efficiency displayed by molybdenum in giving the complete C=C bond oxidative cleavage of alkenes [23, 29].

Results showed an expected increase of the cleavage products in the presence of HCOOH, with a predictable increment of most oxidized products 6 and 7 dependent on the reaction time (Table **1**, entries 6-7). Surprisingly, in the absence of formic acid, selectivity turned in favor of epoxide 2a (81%) with minor amounts of 6 and 7 (Table **1**, entry 8). Based on the well-established sequence of steps with which substrate 1a is known to be oxidized these results seem to indicate that $MoCl_2O_2$ in combination with HCOOH can give very rapidly (within 2 hours) both epoxidation and C=C bond rupture, while in the absence of formic acid the latter process (paths *c* and *d*) is slowed down (Scheme **2**).

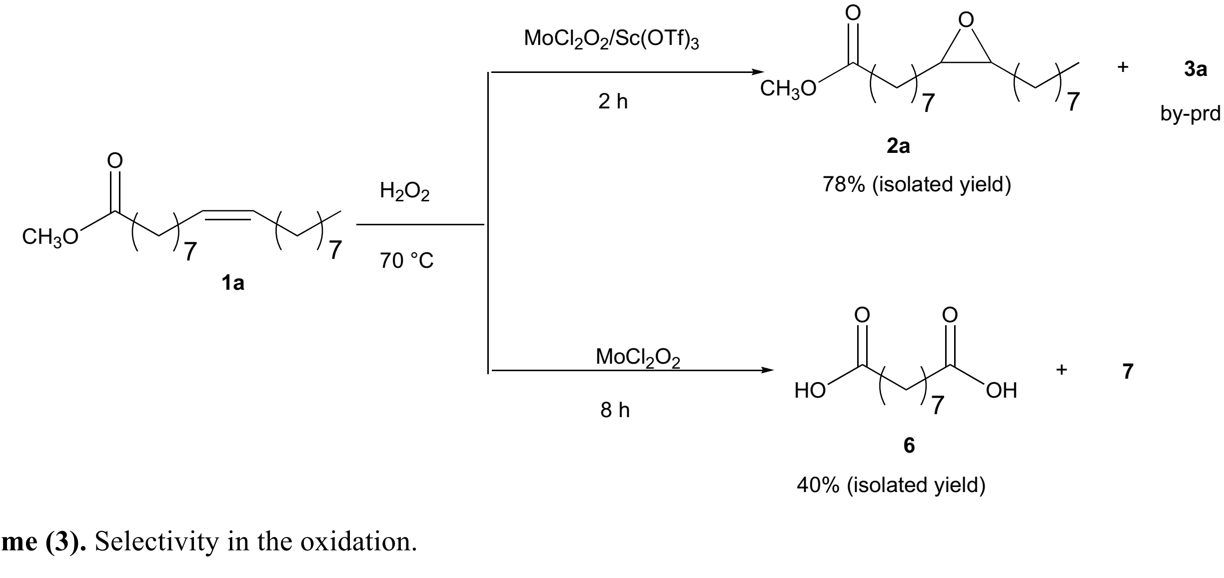
Remarkably, prolonging the reaction times up to 8 hours, epoxide 2a undergoes the almost complete conversion into azelaic acid 6 and pelargonic acid 7 (Table **1**, entry 9), which results in efficient separation by their different partition coefficient between water and ethyl acetate (see par. 3.3) [24], furthermore, during the over-oxidation of the double bond, the hydrolysis of the ester is also observed [6, 30]

Finally, to complete investigations, we evaluated the effect on the selectivity exerted by the combination of the two Lewis acids $MoCl_2O_2$ and $Sc(OTf)_3$ [12]. To our surprise these catalysts, used in an appropriate ratio (1:0.5 mol%), promoted a smooth and rapid (2 hours) conversion of 1a into the epoxide 2a as the main product, producing only little amounts of 1,2-diol 3a and no traces of cleavage compounds (Table **1**, entry 10).

This co-catalytic action by Mo and Sc apparently produces similar effects on the selectivity as



Scheme (2). Step ways mechanism.



Scheme (3). Selectivity in the oxidation.

those observed with scandium triflate alone (Table **1**, entry 5). Instead, a more careful analysis shows that this is a more advantageous reaction, being more rapid and selective (2 hours), and require minor amounts of catalyst.

The results of Table **1** clearly emerged the possibility of governing the selectivity of the oxidation of methyl oleate 1a by choosing properly the combination of catalysts. To validate this protocol, the most effective reactions were repeated on grams scale under conditions suitable to give the epoxidation or the C=C cleavage product 2a and 6, respectively, as depicted in Scheme **3** (see par. 3.2 and 3.3).

Finally, to further assess the efficacy of this method the possibility of recycling the catalyst was verified. Preliminary results evidenced that MoO_2Cl_2 is hard to be reused, as extensively reported in the literature for most of the metal catalysts employed in the cleavage of methyl oleate and oleic acid (*e.g.* for tungsten derivatives [8, 28, 31]. Therefore, recycling experiments were focused on $Sc(OTf)_3$, which in contrast proved to be satisfactorily recycled at least 5 times without lacking its activity under reaction conditions used in entry 5 (see par. 3.1).

CONCLUSION

In conclusion, a flexible method for governing the selectivity in the oxidation of methyl oleate (1a) has been developed by using $MoCl_2O_2$ and $Sc(OTf)_3$ as the catalysts. The protocol possesses several advantages: i) the possibility of obtaining good yields of methyl oleate epoxide 2a or azelaic acid 6, precious industrial intermediates, by simply choosing the combination of Mo and Sc catalysts, ii) the replacement of non-eco-friendly and unrecyclable HBF_4 or H_3PO_4 commonly used in these processes; and iii) the use of simple procedures and less toxic Molybdenum as a catalyst.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's website along with the published article.

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