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Tetrahedron Letters 46 (2005) 3201–3203

Tetrahedron Letters

Ruthenium catalysed oxidation without CCl_4 of oleic acid, other monoenic fatty acids and alkenes

François Zimmermann,[a,b] Eric Meux,[b] Jean-Luc Mieloszynski,[a]
Jean-Marie Lecuire[b] and Nicolas Oget[a,*]

[a]*Laboratoire de Chimie et Applications, EA 3471, Université de Metz, 1 Bd Arago, Metz technopôle, F-57078 Metz Cedex 3, France*
[b]*Laboratoire d'Electrochimie des Matériaux, UMR 7555, Université de Metz, 1 Bd Arago, Metz technopôle, F-57078 Metz Cedex 3, France*

Received 21 January 2005; revised 2 March 2005; accepted 9 March 2005
Available online 25 March 2005

Abstract—Ruthenium catalysed oxidation of alkenes and monoenic fatty acids is reported. The study of the influence of cosolvents (H_2O/MeCN/X) shows that toxic CCl_4 initially used in the Sharpless system (H_2O/MeCN/CCl_4) can be avoided and demonstrates that the oxidative cleavage of C=C bond could be accomplished in good yields with H_2O/MeCN/AcOEt solvent system in a ratio 3/2/2, respectively.

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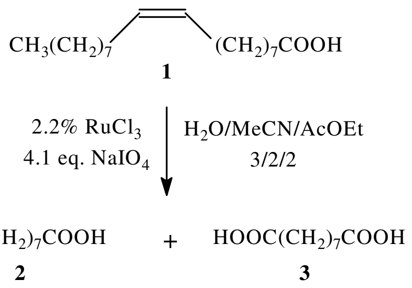
The choice of renewable raw materials for chemical industry is more and more important, to access various finished products and also for economical reasons and ecological effects.[1] For example, the oxidative scission of the double bond converts unsaturated fatty acids to carboxylic and dicarboxylic acids.[2] An industrial application is the production of azelaic acid **3** from oleic acid **1** by ozonolysis.[3] Azelaic acid has a variety of industrial uses: plasticisers, lubricants, cosmetics and painting materials.[4] Pelargonic acid **2** can be used as a corrosion inhibitor.[5] Recently, we have shown that azelaic and pelargonic acids can find applications in wastewater treatment due to the selective precipitation ability of metallic cations.[6] To oxidise oleic acid, metallic oxidants as permanganate can also be used but require a large excess of oxidant and/or the presence of emulsifier.[7] The use of peracetic acid and ruthenium catalysts or H_2O_2 and Mo, W or Re-based catalysts leads to azelaic and pelargonic acids.[8] Other catalytic ways require firstly, the epoxidation or the dihydroxylation of the C=C bond[9] or the metathesis with ethylene of this internal double bond to ω-alkenes.[10] Nevertheless, the catalytic ruthenium system (2.2% $RuCl_3$, 4.1 $NaIO_4$ solvent $H_2O/CH_3CN/CCl_4$ in respective ratio 3/2/2) developed by Sharpless[11] seems more attractive because the yields are better for alkenes and the iodate which is obtained at the end of the reaction can be converted to periodate by electrochemical regeneration.[12,13] However, it is necessary to replace CCl_4 for environmental aspects and industrial considerations.[14] In a recent paper, Schäfer has used the catalytic ruthenium system and showed that toxic cosolvent CCl_4 can be avoided by oxidising the alkenes in an emulsion of water/acetonitrile generated by sonification or by immobilising the alkenes on diatomite.[13]

In this letter, we report the influence of various cosolvents to replace CCl_4 on the oxidation of oleic acid, others monoenic fatty acids and olefins (Scheme 1).



Scheme 1.

Keywords: Ruthenium; Oxidation; Oleic; Fatty acids.

[*] Corresponding author. Tel.: +33 3 87 54 76 51; fax: +33 3 87 54 73 13; e-mail: oget@sciences.univ-metz.fr

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doi:10.1016/j.tetlet.2005.03.052

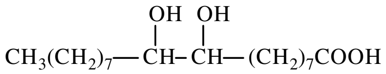
Table 1. Oxidation of oleic acid with $RuCl_3$ (2.2%) and $NaIO_4$ (4.1 equiv) in the presence of cosolvents

Entry	Time	Cosolvents	Ratio	Yield of azelaic[a] (%)
1	4 h 30 min	$H_2O/MeCN/CCl_4$	(3/2/2)	70
2	6 h 30 min	$H_2O/MeCN$	(3/2)	66
3	7 h 30 min	$H_2O/MeCN$	(3/1)	43
4	7 h 30 min	$H_2O/AcOEt$	(3/2)	49
5	4 h	$H_2O/MeCN/AcOEt$	(3/1/3)	67
6	2 h	$H_2O/MeCN/AcOEt$	(3/2/2)	73
7	4 h 30 min	H_2O/MeCN/acetone	(3/2/2)	69
8	48 h	H_2O/MeCN/cyclohexane	(3/2/2)	71

[a] Isolated yields.

When the reaction of oxidation of oleic acid is carried out in the Sharpless conditions (time: 2 h), the oxidative scission of C=C bond is not complete (20% of oleic acid is not oxidised). The conversion of oleic acid to azelaic acid and pelargonic acid is complete for a reaction time of 4 h 30 min (Table 1, entry 1). If the reaction is performed without the cosolvent CCl_4, the reaction time is longer (entry 2). A similar behaviour is obtained with a decrease of the proportion of MeCN (entry 3). Entry 4 shows that MeCN can be replaced to a certain extent but the yields are poorer. These results are usual because Sharpless indicated that CCl_4 have an important role for oxidation and MeCN prevents catalyst inactivation and is crucial for the increased effectiveness and reliability of catalytic RuO_4 oxidation.[11]

The substitution of CCl_4 for another cosolvent is tricky because RuO_4 is a vigorous oxidant and the number of solvent is limited: $CHCl_3$, CH_2Cl_2, ethyl acetate, acetone and cyclohexane are resistant to oxidation by RuO_4.[15] Schäfer showed that the replacement of CCl_4 by $CHCl_3$ or CH_2Cl_2 gave poorer yields of carboxylic acids.[13] Entries 5–8 show that other solvents with a well-judged ratio can be used. The entries 6–8 compare the reaction time and yield of reaction with water, acetonitrile and a third cosolvent (ethyl acetate, acetone or cyclohexane) in ratio 3/2/2, respectively. So, in the view of reaction times and yields, AcOEt appears the better one (entry 6).[16] This is probably attributable to the higher solubility in the solvent system $H_2O/MeCN/AcOEt$ (3/2/2) on the one hand of the reagent oleic acid and the other hand of the resultant vicinal diol **4**, which is rapidly oxidised by $NaIO_4$ in the desired azelaic and pelargonic acids.



$CH_3(CH_2)_7-\overset{OH}{CH}-\overset{OH}{CH}-(CH_2)_7COOH$

4

Azelaic acid and pelargonic acid are extracted by AcOEt and after evaporation of solvent, these two acids are easily purified in water. Azelaic acid is very soluble in warm water (but practically insoluble in cold water) whereas pelargonic acid is insoluble.[17] Two steps of purification[18] give the pure azelaic acid as a white powder (yield: 73%).[19] The typical procedure of the oleic acid oxidation is reported in the references.[20]

Table 2 shows that the oxidation of various alkenes with $NaIO_4$ 4.1 equiv, $RuCl_3$ 2.2%, $H_2O/MeCN/AcOEt$ (3/2/2) is efficient, rapid and mild.[21] 1-alkene (entries 1 and 8), cycloalkenes (entries 3–5) and alkenes with *Z*- or *E*-configuration (entries 2–6) were oxidised in good yields. Oxidative cleavage of the C9–C10 bond of phenanthrene (entry 7) produced diphenic acid in 36% (without the aid of aminomethyl phosphonic acid which is necessary with Na_2WO_4/H_2O_2).[22] Monoenic fatty acids (entries 9–12)

Table 2. Oxidation of alkenes with $RuCl_3$ (2.2%) and $NaIO_4$ (4.1 equiv) in $H_2O/MeCN/AcOEt$ (3/2/2)

Entry	Alkene	Time	Acid product	Yield of acid[a] (%)	Yield of esters[b] (%)
1	1-Decene	4 h	Pelargonic	98	95
2	(*E*)-5-Decene	2 h	Valeric	76	78
3	Cyclohexene	30 min	Adipic	91	90
4	Cyclooctene	2 h	Suberic	90	87
5	1-Methylcyclohexene	2 h	5-Oxohexanoic	85	81
6	Norbonylene	30 min	Norcamphoric	93	82
7	Phenanthrene	2 h	Diphenic	36	42
8	10-Undecylenic acid	2 h	Sebacic	78	81
9	Oleic acid	2 h	Azelaic	73	73
			Pelargonic	65	69
10	Petroselenic acid	2 h	Adipic	47	71
			Lauric		29
11	Palmitoleic acid	2 h	Azelaic	75	73
			Heptanoic		11
12	Erucic acid	2 h	Brassylic	52	65
			Pelargonic		54

[a] Isolated yields.

[b] Isolated as methyl or dimethyl esters ($SOCl_2$, MeOH) and purified by flash chromatography (Et_2O/petroleum ether form 1:10 to 1:1) on silica gel.

lead to carboxylic and dicarboxylic acids in relatively good yields. This oxidation can be performed in a larger scale with the same reaction times and yields.[23]

In conclusion, the toxic carbon tetrachloride initially used in the Sharpless system can be avoided and replaced with ethyl acetate in maintaining catalytic ruthenium oxidation. The oxidative cleavage of the C═C bond of alkenes is accomplished in good yields with H_2O/MeCN/AcOEt solvent system in a ratio 3/2/2 and this method is efficient especially to produce dicarboxylic acids from monoenic fatty acids. Studies are in progress in our laboratories to complete this oxidative system with the regeneration of the oxidants.

Acknowledgements

We are grateful to the ADEME (French Environment and Energy Management Agency) and Regional council of Lorraine for financial support.

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16. The deviations from this solvent ratio led to slower reactions and poorer yields.
17. Solubility of azelaic acid in water at 23 °C is $1.4\ \mathrm{g\,L^{-1}}$; solubilities of azelaic and pelargonic acids in warm water (80 °C) are, respectively, 154.4 and $0.6\ \mathrm{g\,L^{-1}}$; detailed in Ref. 6b.
18. One step of purification gives azelaic acid in 87% yield with 91% purity (pelargonic acid is the only impurity).
19. The resulting insoluble in water corresponds to pelargonic acid as colourless oil.
20. Typical procedure: flask is charged with a magnetic stirred, 3 mL of water, 2 mL of acetonitrile, 2 mL of ethyl acetate, 282 mg (1 mmol) of oleic acid and 877 mg (4.1 equiv) of sodium metaperiodate. To this biphasic solution, 5 mg (2.2 mol %) of ruthenium trichloride hydrate was added and the entire mixture was stirred vigorously for 2 h at room temperature. The mixture was extracted with AcOEt (3 × 10 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated. The resulting material was purified in warm water. Pelargonic acid (65%): ^1H NMR ($CDCl_3$/TMS, 250 MHz): δ 11 (1H, s), 2.3 (2H, t, $J = 7.5$ Hz), 1.6 (4H, m), 1.3 (8H, m), 0.9 (3H, t, $J = 6.1$ Hz); ^{13}C NMR ($CDCl_3$/TMS): δ 180.7, 34.3, 31.9, 29.3, 29.2 (2C), 24.8, 22.7, 14.1; FT-IR (CCl_4): 1712 $\mathrm{cm^{-1}}$. Azelaic acid (73%): ^1H NMR (DMSO-d_6/TMS, 250 MHz): δ 11.9 (1H, s), 2.2 (4H, t, $J = 7.4$ Hz), 1.5 (4H, m), 1.2 (6H, m); ^{13}C NMR (DMSO-d_6/TMS): δ 174.4 (2C), 33.7 (2C), 28.4 (2C), 28.5, 24.5 (2C); FT-IR (KBr) 1701 $\mathrm{cm^{-1}}$.
21. All products gave satisfactory spectral data in agreement with the assigned structure. As example see Ref. 18 for azelaic and pelargonic acids. For the methyl esters: methyl nonanoate: ^1H NMR ($CDCl_3$/TMS, 250 MHz): δ 3.7 (3H, s), 2.3 (4H, t, $J = 7.5$ Hz), 1.6 (4H, m), 1.3 (6H, m), 0.9 (3H, t, $J = 6.2$ Hz); ^{13}C NMR ($CDCl_3$/TMS): δ 174.2, 51.4, 34.2, 32.0, 29.4, 29.3, 29.2, 25.1, 22.8, 14.1; FT-IR (CCl_4) 1740 $\mathrm{cm^{-1}}$; GC–MS (70 eV) *m*/*z*: 172 (2), 141 (9), 87 (41), 74 (100). Dimethyl azelate: ^1H NMR ($CDCl_3$/TMS, 250 MHz): δ 3.7 (6H, s), 2.3 (4H, t, $J = 7.4$ Hz), 1.6 (4H, m), 1.3 (6H, m); ^{13}C NMR ($CDCl_3$/TMS): δ 174.1 (2C), 51.4 (2C), 34.1 (2C), 29.0 (3C), 24.9 (2C); FT-IR (Film) 1737 $\mathrm{cm^{-1}}$; GC–MS (70 eV) *m*/*z*: 216 (0.5), 185 (45), 152 (100), 124 (24), 111 (54), 83 (62), 74 (76), 55 (54).
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23. For example, the oxidation of oleic acid in 10-fold larger scale (oleic acid (2.28 g), $NaIO_4$ (8.77 g), $RuCl_3$ (50 mg) in 30 mL H_2O, 20 mL MeCN and 20 mL AcOEt with magnetic stirred, 2 h) gives after purification pure azelaic acid in 75% yield (1.42 g).