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Catalytic oxidative cleavage of olefins by RuO_4 organic solvent-free under ultrasonic irradiation

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ABSTRACT

All the works reported about oxidative cleavage of olefins by the $RuCl_3/NaIO_4$ catalytic system have been performed in biphasic water/organic solvent(s). The first organic solvent-free oxidation of C=C double bond by 2% $RuCl_3$/4.1 equiv $NaIO_4/H_2O$ is described here using both the emulsifier Aliquat® 336 and 20 kHz ultrasonic irradiation.

1. Introduction

Ruthenium tetroxide is a powerful oxidant in organic synthesis for the oxidative cleavage of olefins and oxidation of alcohols, ethers, and alcynes.[1] RuO_4 is generated in situ by the reaction between $RuCl_3$ (or RuO_2) and $NaIO_4$.[2] Usually, this strong oxidant is used in a catalytic amount of ruthenium in biphasic media water/organic solvent(s). The co-oxidant $NaIO_4$ can be electrochemically regenerated[3] and replaced by HIO_4,[4] NaOCl,[5] or $NaBrO_3$.[6] The most widely used mixture of solvents with 2.2% $RuCl_3$/4.1 equiv $NaIO_4$ is described by Sharpless: $H_2O/MeCN/CCl_4$ in respective ratio 3:2:2.[7] Sharpless underline the important role of (i) carbon tetrachloride for RuO_4 solubilization and (ii) acetonitrile to avoid the catalytic cycle inactivation due to low-valent ruthenium carboxylate complexes.[8] For these considerations and others (because RuO_4 is a vigorous oxidant, the number of co-solvents is limited),[9] the substitution of CCl_4 or MeCN by another co-solvent is not easy. Nevertheless, depending on the reactants and the oxidation products (epoxide, diol, ketol, dione, aldehyde, or acid), the mixture of solvents, their ratio and reaction times must be modified. When the reaction was carried out in a short time (0.5 min) at 0 °C in H_2O/CH_3CN/AcOEt, the *cis*-dihydroxylation of cyclohexene occurred selectively.[10] Moreover at room temperature, hexanedial was obtained in $ClCH_2CH_2Cl/H_2O$ (5:1) with nano-RuHAP[11] while adipic acid was the only product remaining in H_2O/CH_3CN/AcOEt (3:2:2) after 30 min[12] or in H_2O/CH_3CN (7:1) with sonification for several hours.[13]

To our knowledge, all the olefin oxidations by $RuCl_3/NaIO_4$ were carried out in aqueous media (binary or ternary water/organic solvent mixtures). To minimize the environmental impact resulting from organic solvent use, aqueous reactions are searched for economical reasons and/or required.[14] Furthermore, the application of ultrasonic irradiation in catalytic reactions promotes advantages such as enhancement of chemical reactivity, good yields, short reaction times, and mild reaction conditions.[15] But can water be the unique solvent with a $RuCl_3/NaIO_4$ catalytic system under ultrasonic irradiation? In a previous study about oleic acid oxidation, we showed that ultrasound and the presence of an emulsifier allowed the oxidative cleavage in aqueous media (water >50% v/v).[16] In this Letter, we report the first results of catalytic oxidation by RuO_4 organic solvent-free, in water, under 20 kHz sonochemical irradiation and the presence of Aliquat® 336.

2. Results and discussion

Usually, to obtain the oxidative cleavage of alkene by the catalytic system $RuCl_3/NaIO_4$, 4.1 equiv of $NaIO_4$ is needed and the optimal ratio $RuCl_3 \cdot xH_2O$/alkene is 2% mol[17] (Scheme 1). The total conversion of alkene was indicated by the persistent yellow color of the mixture due to the presence of RuO_4.[18] This was checked by the GC-analysis and by the absence of ethylenic signals in ^1H and ^{13}C NMR. The oxidation in water was firstly experimented with 1-decene as the model substrate.[19] Table 1 shows that the 1-decene total conversion was obtained in biphasic water/organic

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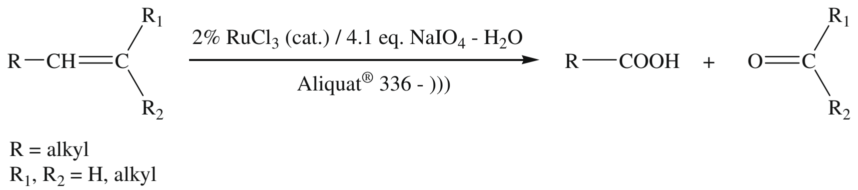

Scheme 1. Olefin oxidative cleavage by $RuCl_3/NaIO_4$—2% Aliquat® 336 in water with US.

Table 1
Oxidative cleavage of 1-decene with 2% $RuCl_3$/4.1 equiv $NaIO_4$

Entry	Solvent mixture	Ratio	US	Aliquat® 336	Reaction time (min)	Pelargonic acid yield[a] (%)
1	$H_2O/CH_3CN/CCl_4$	3:2:2	—	—	120	89[b]
2	H_2O/CH_3CN/AcOEt	3:2:2	—	—	240	99
3	H_2O/CH_3CN	7:1	—	—	15	85–92[c]
4	H_2O/CH_3CN	1:1	)))	—	10	85
5	H_2O/CH_3CN	1:1	)))	2%	5	92
6	H_2O	—	—	—	300	25[d]
7	H_2O	—	—	—	20	4[e]

[a] Isolated yields.
[b] See Ref. 7.
[c] 1-Decene adsorbed on diatomite see Ref. 13.
[d] Analytical GC proportions of crude product, side-products: 11% nonanal, 64% 1,2-decanediol.
[e] Analytical GC proportions of crude product, only 9% of 1-decene conversion.

solvent mixtures and led to high yields of pelargonic acid (entries 1 and 2). The binary mixture H_2O/MeCN could be used with an activation of 1-decene absorbed on diatomite (entry 3) or by 20 kHz ultrasonic irradiation (entry 4). With the emulsifier Aliquat® 336 (2%) in H_2O/MeCN under ultrasound (US), the oxidation led to a 92% pelargonic acid yield in 5 min (entry 5). But when water was the unique solvent (entry 6), after 5 h, pelargonic acid (25%) was obtained with other oxidation compounds: nonanal (11%), 1,2-decanediol (64%). This amount of 1,2-decanediol is surprising because 1,2-diols are easily cleaved under mild conditions with periodate. If the reaction time was 20 min (entry 7), the conversion of 1-decene was only 9% (4% pelargonic acid yield). Entries 6 and 7 show that despite its solubility (2% w/v at 20 °C),[20] RuO_4 is not efficient in water for the oxidative cleavage of alkene.

When ultrasonic irradiation was replaced by magnetic stirring, after 20 min, the conversion of 1-decene was 15% (Fig. 1). The addition of Aliquat® 336[21] allowed a better conversion of 1-decene to the oxidation compounds (pelargonic, nonanal, and 1,2-decanediol). The presence of 1,2-decanediol could be due to the hydrolysis of the ruthenate ester intermediate and the oxidative cleavage of this by $NaIO_4$ generates nonanal.[13] The total conversion of 1-decene was reached with 2% Aliquat® 336 in 20 min and with a larger amount, no evolution was observed. With 2% Aliquat® 336 and US (Fig. 2), no 1,2-decanadiol was detected. 1-decene was first cleaved into nonanal which was then oxidized to pelargonic acid. After 20 min, no 1-decene was detected by GC/MS and after 30 min, only pelargonic acid was found (76% yield, Table 3, entry 1).

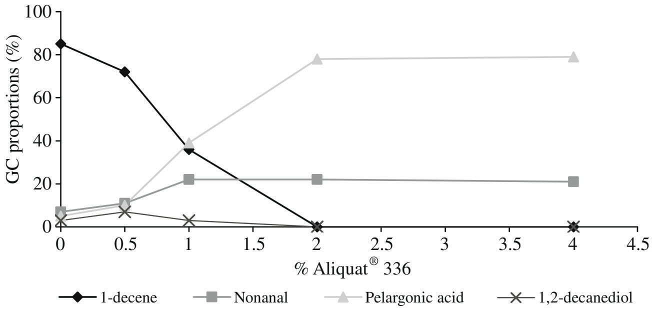

Figure 1. 1-Decene oxidative cleavage with 2% $RuCl_3$/4.1 equiv $NaIO_4$—x% Aliquat® 336—H_2O—US (20 min) monitored by GC/MS.

Table 2 shows the effects of the Aliquat® 336 and/or ultrasound on 1-decene oxidation reaction in water after 20 min with 2% $RuCl_3$/4.1 equiv $NaIO_4$. When the cleavage was performed with magnetic stirring (entry 1) the conversion was only 9%. If ultrasonic irradiation or Aliquat® 336 was added (entries 2 and 3), the conversion increased slightly to 15% and 27%, respectively. But when ultrasound and Aliquat® 336 were associated (entry 4), the conversion was completed within 20 min and led to a 76% pelargonic acid yield in 30 min. This demonstrates the synergy between Aliquat® 336 and ultrasound which brings on a rapid oxidative cleavage of 1-decene.

The system 2% $RuCl_3$/4.1 equiv $NaIO_4$—2% Aliquat® 336—20 kHz US was extended to the oxidation of other olefins in water (Table 3). The total conversion of alkenes (*Z*, *E*) and cycloalkenes was reached rapidly after 15–35 min (entries 1–7) and the carboxylic acids and diacids were obtained in good yields (65–93%). Owing to the high solubility of 9-decenoic and 10-undecenoic acids in water, their oxidations were fast and efficient (entries 8 and 9). However, the reaction of fatty oleic acid needed a longer time and led to 62% azelaic acid and 98% pelargonic acid yields (entry 10). Regarding yields, the difference between azelaic and

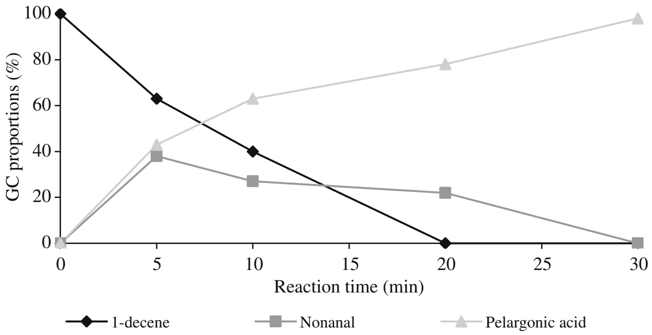

Figure 2. 1-Decene oxidation with 2% $RuCl_3$/4.1 equiv $NaIO_4$—2% Aliquat® 336—H_2O—US monitored by GC/MS.

Table 2
Oxidative cleavage of 1-decene with 2% $RuCl_3$/4.1 equiv $NaIO_4$—H_2O in 20 min

Entry	Aliquat® 336	Ultrasound	Reaction time (min)	Conversion (%)	Pelargonic acid[a] (%)
1	—	—	20	9	5
2	—	)))	20	15	5
3	2%	—	20	27	17
4	2%	)))	20	100	76

[a] Analytical GC proportions of crude product.

Table 3
Olefin oxidation with 2% $RuCl_3$/4.1 equiv $NaIO_4$—2% Aliquat® 336—H_2O—US

Entry	Reactant	Product	Reaction time (min)	Yield[a] (%)
1	1-Decene	Pelargonic acid	30	76
2	E5-Decene	Valeric acid	15	74
3	1-Methylcyclohexene	6-Oxoheptanoic acid	15	74
4	Cyclohexene	Adipic acid	20	81
5	Cycloheptene	Pimelic acid	15	65
6	Cyclooctene	Suberic acid	30	93
7	Norbornene	Norcamphoric acid	35	75
8	9-Decenoic acid	Azelaic acid	30	96
9	10-Undecenoic acid	Sebacic acid	45	85
10	Oleic acid	Azelaic acid	480	62[b]
		Pelargonic acid		98[b]

[a] Isolated yields.
[b] The separation and purification of mono- and diacids are described in Ref. 16.

Table 4
Oxidation of other functions with 2% $RuCl_3$/x equiv $NaIO_4$—2% Aliquat® 336—H_2O—US

Entry	Reactant	Product	Equiv $NaIO_4$	Reaction time (min)	Yield[a] (%)
1	1-Nonanol	Pelargonic acid	2	30	58
2	2-Nonanol	2-Nonanone	2	15	89
3	Dibenzylsulfide	Dibenzylsulfone	1	60	80
4	THF	γ-Butyrolactone	4.1	60	6[b]

[a] Isolated yields.
[b] Analytical GC proportions of crude product: 94% THF, 6% γ-butyrolactone.

pelargonic acids was attributed to the extraction of the acids by AcOEt and purification.[22]

Other organic functions were oxidized by $RuCl_3/NaIO_4$ catalytic system (Table 4) with the theoretical amount of $NaIO_4$ necessary to oxidize the reactant. Reactions with alcohols (entries 1 and 2) were performed with 2 equiv $NaIO_4$ and led to an 89% 2-nonanone yield for 2-nonanol. Concerning 1-nonanol, the low yield (58%) was explained by a side reaction between pelargonic acid and 1-nonanol to produce nonyl pelargonate. Dibenzyl sulfide was also oxidized in 60 min with 1 equiv $NaIO_4$ into dibenzyl sulfone (entry 3). But the oxidation of THF to γ-butyrolactone was not efficient in spite of the 4.1 equiv $NaIO_4$ used (entry 4). The oxidation of benzylmethylether was performed with 2 equiv $NaIO_4$ and the proportion of final products was monitored by GC/MS (Fig. 3). In contrast to biphasic aqueous/organic solvent mixtures,[7,23] which led only to methyl benzoate, we have mainly noted the formation of benzoic acid. The presence of benzaldehyde suggests the hydrolysis of benzylmethylether into benzyl alcohol, itself oxidized to benzaldehyde and then to benzoic acid. This reaction is in competition with the formation of methyl benzoate whose amount decreased during the experiment. This suggests a hydrolysis of methyl benzoate in water under ultrasonic irradiation too.

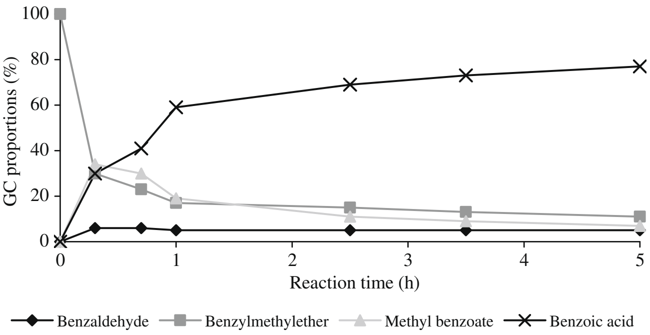

Figure 3. Benzylmethylether oxidation with 2% $RuCl_3$/2 equiv $NaIO_4$—2% Aliquat® 336—H_2O—US monitored by GC/MS.

3. Conclusion

In summary, we have reported the first results of the efficient oxidative cleavage of olefins, in water, with the catalytic system 2% $RuCl_3$/4.1 equiv $NaIO_4$ whereas this oxidation reaction had been described in biphasic water/organic solvent(s). Of course, all the oxidation product yields are not up to the level of those obtained in biphasic water/organic solvent(s),[1,7,12,16] but our results demonstrate that $RuCl_3/NaIO_4$ catalyst can be used in water for environmentally benign reactions. The new reaction condition is due to the concomitant use of 2% Aliquat® 336 and 20 kHz ultrasonic irradiation. The application of this condition for other organic compounds (especially those soluble in water) and the reasons behind the synergy between Aliquat® 336 and US are currently under investigation.

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mixture was exposed to ultrasonic irradiation at room temperature for 30 min. After the addition of H_2SO_4 2 M (0.5 mL), the aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was dissolved in a 5% sodium hydroxide solution, extracted with ether (2 × 10 ml), and acidified with concentrated H_2SO_4 2 M until pH 1. This solution is extracted with ethyl acetate (3 × 10 mL) and the combined organic phases were dried ($MgSO_4$), filtered, and concentrated to give 76% yield purified pelargonic acid (120 mg). The GC-analysis showed pelargonic acid was the unique product and spectral data were in agreement with the assigned structure. ^{1}H NMR (250 MHz, $CDCl_3$) δ 11.0 (s, 1H), 2.3 (t, 2H, $J = 7.5$ Hz), 1.6 (m, 2H), 1.3 (m, 10H), 0.9 (t, 3H, $J = 6.1$ Hz). ^{13}C NMR (63 MHz, $CDCl_3$) δ 180.7 (COOH), 34.3 (CH_2–COOH), 31.9, 29.3, 29.2 (2C), 24.8, 22.7, 14.1 (CH_3). IR (Film) (ν_{max}/cm^{-1}): 1720 ($C{=}O$). GC–MS [Instrument: Perkin–Elmer GC Autosystem XL—Clarus 500; carrier gas: He, flow rate: 0.75 mL/min; column: Elite 5MS, 5% diphenyl/95% dimethylpolysiloxane, temp = 60–300 °C (10 °C/min), inj. temp = 200 °C]: $t_R = 10.89$ min; MS (EI, 70 eV): m/z (%): 158 ($M^{\bullet+}$, 2), 129 (18), 115 (23), 98 (15), 87 (12), 73 (80), 69 (22), 61 (13), 60 (100), 57 (62), 55 (45), 43 (47), 41 (51), 39 (19).

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