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Authors: Boris Guicheret, Yann Bertholo, Philippe Blach, Yann Raoul, Estelle Metay, and Marc Lemaire

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201801640

Link to VoR: http://dx.doi.org/10.1002/cssc.201801640



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A two-step oxidative cleavage of 1,2 diol fatty esters into acids or nitriles *via* a dehydrogenation-oxidative cleavage sequence

Boris Guicheret,^[a] Yann Bertholo,^[a] Philippe Blach,^[b] Yann Raoul,^[b] Estelle Métay*,^[a] Marc Lemaire^[a]*

Dedication ((optional))

Abstract: The dehydrogenative oxidation of vicinal alcohols catalysed by a commercially $64w\%Ni/SiO_2$ catalyst leads to the formation of α -hydroxyketone. This first step was developed without additional solvent according to two protocols: "under vacuum" or "with an olefin scavenger". The synthesis of ketols was carried out with good conversions and selectivities. The recyclability of the supported nickel was also studied. Acyloin was then cleaved with oxidative reagent "formic acid-hydrogen peroxide" mixture, cheap and used in large scale for oxidation industrial process. The global yield of this sequential system was up to 80% to pelargonic acid and azelaic acid mono methyl ester without intermediate purification. By treating the acyloin intermediate with hydroxylamine, nitriles were obtained with a good selectivity.

Introduction

In recent years, attractive tools were developed to convert biomass to consumer products. Among the abundant renewable feedstock, oils are notably converted into fatty esters or acids which are modified for lubricant, solvent or plasticizer applications.¹ Another part is dedicated to the production of biodiesel from the methanolysis of vegetable oils.² The portion of biodiesel into diesel is ordered by the European directives which are at the moment fixed at 7%. These part could be reduced with keeping a similar production, thus the valorisation of these derivatives constitutes a challenging research program. One alternative may concern the modification of the C-C double bond by an oxidative cleavage to acid building blocks.³ From oleic derivatives, such transformation allows the formation of azelaic (AA) and pelargonic acids (PA). The main oxidative transformation of oleic acid (OA) to AA and PA is carried out by ozonolysis.⁴ It was also noticed that treatment of the ozonide intermediate with hydroxylamine hydrochloride provides a mixture of acids and nitriles (nonanenitrile PN and 8-cyanooctanoic acid

 [a] Dr. Boris Guicheret, Yann Bertholo, Dr. Estelle Métay, Prof. Marc Lemaire
 ICBMS-UMR 5246 – Université Lyon 1 – CNRS – INSA – ESCPE Bâtiment Lederer – 69622 Villeurbanne Tel : 04 72 44 85 07 E-mail: estelle.metay@univ-lyon1.fr
 [b] Dr. Philippe Blach, Dr. Yann Raoul

Oleon, Avril Group Rue les Rives de l'Oise, 60280 Compiègne

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Figure 1. Classical pathways for the synthesis of azelaic and pelargonic acids.

ACO).5 Currently, the use of toxic ozone and explosive intermediate is in balance with the efficiency of the process in term of productivity and atom economy. From a general point of view, two main strategies can be considered to synthesize azelaic and pelargonic acids from oleic acid (figure 1).³ Considering the direct oxidative cleavage (route A) of the carbon-carbon double bond, ozonolysis is probably the most efficient way to produce the desired acids. Alternatives were developed, as for example the use of stoichiometric oxidant (nitric acid⁶ or KMnO4⁷) but these reagents can damage the material by corrosion and generate a large amount of salts. Catalysts, such as osmium tetroxide⁸ or ruthenium tetroxide⁹ associated with sodium periodate were also efficient for the acid formation. Other systems, further to the studies of Ishii¹⁰ and Venturello¹¹, were developed using hydrogen peroxide associated with homogeneous metal as rhenium,12 ruthenium,13 iron14 or ammonium/polyoxometalate.15 In the latter case, the polyperoxometalates used generally contain tungstic acid as active metal oxide. These systems were able to cleave a carbon-carbon double bond with an excess of hydrogen peroxide (5 eq). The polyoxometalate-H₂O₂ olefin cleavage mechanism supposes several intermediates including aldehydes (perhydrolysis of epoxide) or alpha hydroxyketone and diketone by successive oxidation of the diol.¹¹ An efficient system (polyoxometale-H2O2) leads to azelaic acid derivatives and pelargonic acid with 80% yield. The weak point of these conditions concerns the recycling of the catalytic system, but some recent results seem promising.¹⁶ Two Heterogeneous catalyst systems in the presence of hydrogen peroxide have also been reported recently by Do, one with tungsten oxide nanoparticules and the other one with molybdenum oxide.¹⁷ The indirect oxidative cleavage (route B) was also studied. Kockritz has reported an efficient Au/Al₂O₃-O₂ system in basic conditions to cleave 9,10dihydroxystearic acid (DHSA) to PA and AA in 90% yield.¹⁸ A company have related a homogeneous cobalt-air¹⁹ system able to produce 80% yield of PA and AA from DHSA. Our group has

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also reported the oxidation of DHSA by bleach without added metal.²⁰ A mechanistic study concerning the oxidative cleavage of diols mentioned that α -hydroxyketone and diketone compounds are key intermediates notably with a gold catalyst.²¹ Another group recently employed a combination of Pt/C and V2O5 to cleave cyclohexanediol and proposed also the corresponding ketol as intermediate.²² However, the access of such compounds was poorly described in the literature. One reference reports the use of KMnO₄ in dilute and pH controlled conditions which modified directly OA to the desired acyloin function.23 Epoxystearate was also converted to ketol in DMSO in the presence of catalytic BF3-Etherate.24 Recently, we have developed a procedure for the dehydrogenation of diols into acyloins using Ru/C.25 The access to α-hydroxyketone is important as this motif could be converted into aldehydes by a retro-acyloin reaction catalysed by a thiazolium catalyst.²⁶

In this report, we describe a two-step procedure dealing first with a dehydrogenation to prepare a ketol followed by an oxidation to synthesise carboxylic acids from diols or a treatment with hydroxylamine hydrochloride to obtain nonanenitrile PN and methyl 8-cyanooctanoate MCO. We have demonstrated that vicinal alcohols and more precisely 9,10-dihydrostearic acid mono methyl ester could be selectively dehydrogenated to α -hydroxyketone by Ru/C. Regarding the price of ruthenium, the use of other metals was considered.



Figure 2. Consecutive oxidative cleavage of DHSE strategy.

Results and Discussion

To our knowledge, the transformation of diols to ketols catalysed by a low price heterogeneous metal was only described for the synthesis of dihydroxyketone (DHA) in gas phase.²⁷ In addition, the dehydrogenation of secondary and primary alcohols respectively to ketones and aldehydes has known a large interest from the last ten years. Cu/Al₂O₃,²⁸ Ni/Al₂O₃,²⁹ Ag/Al₂O₃,³⁰ Raney Nickel³¹ and La-Cu/MgAlO³² are efficient system to convert 2octanol to 2-octanone. To shift the equilibrium, styrene was added in some cases, as a hydrogen scavenger.³¹

For this study, the 9,10-dihydroxystearic acid mono-methyl ester DHSE was used as a model benchmark to carry out the dehydrogenation step. The mono-dehydrogenation of DHSE using nickel catalyst was explored. At the beginning, nickel and copper sponge were compared to 64w%Ni/SiO₂. Experiments were accomplished in 100 mL schlenk. As nickel and copper sponge are in suspension in water, they were washed 8 times with MilliQ water and the pH was adjusted to neutral.



[a] Reaction conditions: 100 mL Schlenk flask fitted with a condenser, 6 mmol of 1. [b] Determined by GC and H-NMR.

Then the catalyst was dried using isopropanol and vacuum. The residual catalyst powder was weighted and the corresponding mass of the starting material was introduced with the ratio 3: 1 respectively diol: catalyst. The reactor was heated to 175 °C under argon then connected to vacuum at 10mbar. After four hours reaction, 1 was partially converted into the desired KA with a good selectivity using copper sponge (Table 1, entry 1). Unfortunately, the appearance of the catalyst was modified at this temperature as orange copper aggregates were observed in the crude mixture. The nickel catalysts (Table 1, entry 2-3) have displayed a higher efficiency compared to copper as both nickel catalysts allowed to reach high conversions in 4 hours, 95% and 99% respectively for sponge nickel and nickel on silica. The selectivity for 1a reached 80% and approximately 10% of diketone were also identified. Similar results were obtained with both nickel catalysts. The reaction time was then optimized with 64%wNi/SiO2. The first objective was to determine when the diketone co-product was formed. Surprisingly, when the reaction was stopped after 1 hour only 3% conversion was observed by GC and after four hours reaction, the result was the same as before (table 1, entry 3).

Table 2. Determination of the activation time of the catalyst.					
	 Metal / support 35 mol solvent free H₂ Activation time vacuum = 10 mbar 30min, 175 °C 	% ++++++++++++++++++++++++++++++++++++	0 7 7 1 1 1:1 m	1c	
Entry	Activation time (min) ^b	Conv. of 1 ^[c] (%)	Sel. 1a ^[c] (%)	Sel. 1b-1c ^[c] %	
1	No	3	98	-	
2	10	31	96	1-0	
3	15	86	97	1-1	
4	30	93	96	1-1	

[a] Reaction conditions: 100 mL Schlenk flask fitted with a condenser, 6 mmol of **1**. [b] Activation: H_2 balloon in a schlenk containing DHSE, catalyst at 175°C. Reaction time = activation time+30 min under vacuum (10 mbar). [c] Determined by GC and ¹H-NMR.

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Table 3. Influence of the quantity of the catalyst.

OH 0 7 0H 7 0H 7 1	O Metal / support mol% solvent free 30 min H ₂ activation time, vacuum = 10 mbar, 1-2h 175 °C	1:1 mixture of regioisomer	0 0 7 + 7 1b 1:1 mixture	0 7 1c of regioisomer
Entry	^{64w%} Ni/SiO₂ mol%	Conv. of 1 ^{[c} (%)	^{:]} Sel. 1a ^[c] (%)	Sel. 1b-1c ^[c] %
1 ^[b]	2.5	33	94	Traces
2 ^[b]	5	77	95	Traces
3	10	74	92	Traces
4	20	87	96	2-1
5	35	93	97	1-1

[a] Reaction conditions: 100 mL Schlenk flask fitted with a condenser, 6 mmol of 1. Activation: H₂ balloon in a schlenk containing DHSE, catalyst at 175°C. Reaction time = activation time+1h under vacuum (10 mbar). [b] 2h under vacuum. [c] Determined by GC and ¹H-NMR.

The catalyst activation occurs during the process. To clarify this point, the reaction mixture was set up under hydrogen gas during a fixed time. After this activation time, H_2 was continuously removed under vacuum and the crude stirred for 30 min at 175°C. 10 min was too short to reach high conversion (Table 2, entry 2). In fact, 31% DHSE 1 was converted to ketol (96% sel.) and diketone **1b** (traces). No monoketone **1c** was observed.

A longer activation time (Table 2, entry 3-4) allowed to obtain more than 85% conversion with the same selectivity in favour of the desired product **1a**. Finally, the best result was obtained after 30 min under hydrogen, but the vacuum is necessary at this point as only 10% of ketol were measured before pumping.

The required quantity of catalyst was then evaluated. With 2.5 and 5 mol% (Table 3, entries 1-2), the duration of the reaction was longer giving respectively 33 and 77% conversion of DHSE with 94% selectivity for **1b**.

Table 4. Optimization of 1-decene equivalences.					
	^{64w%} Ni/SiO ₂ 35 mol% solvent free 20 min H ₂ Activation time 1-decene 1 2h20, 175 °C	0 7 0 H 7 7 H 7 7 7 7 7 7 7 7 7 7	0 7 7 1b 1:1 mixt	1c ure of regioisomer	
Entries	1-decene	Conv.of 1 ^[b]	Sel. 1a ^[b]	Sel. 1b-1c ^[b]	
	eq.	(%)	(%)	%	
1	No	34	88	6-3	
2	0.5	59	96	1-0	
3	0.8	71	94	3-0	
4	0.9	70	94	3-0	
5	1	70	92	3-1	
6	1.1	33	81	6-3	
7	1.1	99	94	1-1	
8	1.2	5	40	20-20	

[a] Reaction conditions: 100 mL Schlenk flask fitted with a condenser, 6 mmol of 1. Activation: H_2 balloon in closed schlenk containing DHSE, catalyst at 175°C. 1-Decene was added with a syringe pump. Reaction time = activation time + 2 hours in closed schlenk. [b] Determined by GC and ¹H-NMR.

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A larger quantity (10 mol%) leads to the same result but the time was decreased to one hour. With larger quantities of nickel, the selectivity stays high (96%) (Table 3, entry 4-5) and good conversions were observed. The elimination of hydrogen under vacuum is limited to high boiling point starting material, as a consequence, we explored the introduction of an olefin as hydrogen scavenger and carried out the transformation in a closed reactor. 1-Decene in reason of its boiling point was evaluated as hydrogen scavenger. The activation of the catalyst under hydrogen was accomplished for 20 min before the introduction of 1-decene. With a low quantity of hydrogen scavenger (Table 4, entry 2), the conversion was not completed but the reaction was selective (96%) for 1a. With substoichiometric quantity of decene 0.8-0.9-1 eq. (table 4, entry 3-4-5), the conversions were similar for the third (70%). If more olefins were added, no reaction was observed. ¹H-NMR analysis revealed the absence of terminal olefin in the crude. More precisely, isomerisation of the double bond occurred in this case, inhibiting the hydrogen scavenger as the reduction is more difficult. 1-decene was then introduced with a syringe pump for one hour (table 4, entry 7). The conversion of DHSE was complete after 20 min, with 94% selectivity for ketol.



Figure 3. Dehydrogenation of 20g of DHSE using syringe pump 1-decene introduction.

The reaction was carried out from 20 g of starting material (figure 3) and allowed the production of 18.2g of ketol with 95% purity after a fast distillation of decane. On 100 g scale, the preparation of acyloin from DHSE was carried out in a steel autoclave to produce 87g of KA with 90% purity yield after distillation of decane and crystallisation in pentane. 4% diketone **1b**, 2% monoketone**1c** and 4% DHSE were also identified.

The influence of the temperature rapidly demonstrated that 175°C is a good compromise between conversion and selectivity. More precisely, at 160°C a low conversion (20%) was observed. At higher temperatures, 180 and 185°C, the conversion of **1** was close to 80% and the selectivity for 1a 90%, but monoketone **1c** resulting of diol dehydration was also formed.

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Graph 1: Recycling of Nickel silica (Reaction conditions: 100 mL Schlenk flask fitted with a condenser, 6 mmol of **1**. Cat. 190 mg. Activation (20min): H_2 balloon in closed schlenk containing DHSE, catalyst at 175°C. 1.1 eq. of 1-decene introduced after activation time Reaction during 1 hour with a syringe pump. Conv. and Sel. Determined by GC and ¹H-NMR.)



The recyclability of nickel on silica was later studied. The previous conditions developed, with the introduction of olefin with a syringe pump, were repeated five times with the same catalyst. As nickel catalyst are sensitive to air, between each recycling tests, the catalyst was always kept with solvent, then dried in the schlenk and activated under H₂ before each run. The first run was stop before 1 hour due to a heating system failure. The conversion of DHSE was 87% and 85% yield of KA were measured (Graph 1, run 1). From run 2 to 5, conversion of DHSE were higher than 97% in favour of 90% yields of ketol product. The formation of **1b** and **1c** was below 5% yield after each recycling test.

The retained conditions under a reduced pressure (protocol A) or in the presence of a hydrogen scavenger (protocol B) were applied on other substrates in order to evaluate the method. Diols were dehydrogenated according to both protocols, the results are detailed in the following table. Initially, diols from fatty acids were introduced under these dehydrogenation conditions. The diol diester 2 (Table 5, entry 2), 80% purity, was converted at 96% into 2a (90%) by heating under a reduced pressure (method A). The protocol (B) using 1-decene allowed 90% conversion of dihydroxyerucate 3 derived from erucic acid with 96% selectivity for ketol function 3a (table 5, entry 3) in 70% isolated yield. The similar polarity of the ketol 3a and the diketone 3b is responsible of the difference between conversion and isolated yield. Dihydroxycycododecane 4 was also converted under the vacuum protocol and 75% of 2-hydroxycyclododecanone 4a were isolated (Table 5, entry 4). Unexpectedly, cyclohexanediol has shown a different reactivity (entry 5 table 5). Dihydroxycyclohexane was not converted selectively to ketol. A large amount of catechol was also detected by ¹H-NMR. 1,2-octane diol was also poorly reactive and 15% of 1-hydroxy-2-octanone and 5% of 2-octanone were measured by gas chromatography.

OH R KR' OH	^{54w%} Ni/SiO ₂ 0.35 mol% method A or B solvent free H ₂ Activation time 175 °C	R OH a 1:1 mixture of regio	+ R K	[~] R' + 1:1 miz	R c ture of regi	רי Disomer	
Entry	он ^R ↓↓_ _{R'}	Protocol	Conv . (%)	Selecti (isolate	Selectivity – (isolated yield%)		
	ÓН			а	b	с	
1	он о	А	93	90- (80)	4	1	
	7 OH 7 OH 7	В	97	92- <i>(90)</i>	4	-	
2		Α	88	88- (57)	6	3	
	он о	Α	87	88	6	3	
3 77 11 0- 0H 11	OH 11	В	96	90- (<i>70</i>)	3	Trac es	
4	OH	A	82	92- (75)	2	2	
5	ОН	В	10	-	-	-	
6	И ОН	А	25	60	-	20	
	он	В	28	64	-	18	
				5			
7	н5 он	А	99	4	99		

[a] Reaction conditions: Method A: 100 mL Schlenk flask fitted with a condenser, 6 mmol of diols. Activation (20 min): H₂ balloon in closed schlenk containing DHSE and catalyst at 175°C, Reaction time =activation time+1h under vacuum (10 mbar vacuum strategy). Method B: diol 6 mmol, 1-decene 1.1 eq filled by syringe pump in one hour in closed schlenk (Olefin strategy). Conversion and selectivity determined by GC and ¹H-NMR. Isolated yield after flash chromatography.

However the dehydrogenation of secondary alcohols under vacuum in the presence of a nickel catalyst was very efficient (table 5 entry 7). This result is in agreement with other study dealing with the alcohol dehydrogenation with Raney nickel. Nevertheless, Protocol A and B were not efficient to convert primary alcohol, octanol into octanal (table 5 entry 8). Another challenge was dedicated to the evaluation of the reactivity of hydroxylated triglyceride (TGH).

The reaction conditions were modified by the introduction of dodecane to decrease the viscosity of the medium. Although the complexity of the H-NMR 75-80% conversion of vicinal alcohol and 55-60% ketol **TGHD** function formation were determinated. (H-NMR analysis available in supporting information)

Table 5. Dehydrogenation of varied vicinal alcohols

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Figure 4: Formation of ketol from hydroxylated triglyceride



With this efficient tool in hand, the next part of this study was devoted to the cleavage of ketol into carboxylic acid. This transformation can be accomplished with oxidant in stoichiometric quantities generating a large amount of salts.³³ From an atom economy point of view, oxygen is the best oxidant. In several studies, the use of vanadium catalyst is reported with good selectivities for the cleavage to acids or ester.34 Vanadium supported on heterogeneous acids (Nafion, argils) allowed the recovery of the metal.³⁵ Under an oxygen pressure, the cleavage of ketol occurred without catalyst, but in this case, side-reactions were in competition with the selective formation of acid.36 Vanadium lixiviation were also mentioned which explained a low metal recovery and a low turnover number. Hydrogen peroxide was used with methyltrioxorhenium to cleave ketols.³⁷ H₂O₂-KOH was efficient stoichiometric oxidant to react with complex molecules.38

For this study, oxygen was not selected to perform the cleavage but the efficiency of peracids was considered and more precisely the association of hydrogen peroxide and formic acid. Performic acid was commonly used for epoxide preparation in large scale, but also as co-oxidant associated with transition metal.^{12,39,40} The first reaction was accomplished using 10 equivalents of formic acid from 2 g of ketol and 3.5 equivalents of H₂O₂ (Figure 5).

Figure 5. Oxidation of KA to acid in performic acid medium.



This oxidant treatment allowed 95% conversion of Ketol KA and the formation of 90% of pelargonic acid was identified by GC with an internal standard calibration. Only 78% of azelaic acid mono methyl ester **AAM** were detected. The lower quantity of azelaic derivative prompted us to change the extracted solvent substituting ethyl acetate by MTBE (Methyl *tert*-butyl ether) previously employed by Kockritz.^{21b} This modification allowed us to recover additional 4% of azelaic acid **AA**. In these conditions the reaction medium has a monophasic appearance which could be due to the ability of formic acid to solubilise fatty KA in water. The possibility to decrease the quantity of formic acid was then evaluated (Table 6). With 2.5 eq. of formic acid a low conversion was noticed (Table 6, entry 1).

Table 6. Effect of formic acid quantity ^[a]					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					
entry	Formic acid eq.	Conv. ^[b] KA (%)	Selectivity (Selectivity (%) ^[b]	
			PA	AAM-(AA)	
1 ^[c]	2.5	10	30	30-(nd)	
2 ^[c]	5	15	30	30-(nd)	
3	10	95	94	82-(4)	
4 ^[d]	20	95	92	82	

[a] Reaction conditions: KA (2g, 6mmol), $^{30w\%}H_2O_2$ (2.2g, 21 mmol, 3.5 eq. introduced by syringe pump for 1 hour at 30°C), HCOOH (entry 1, 0.7g, 15 mmol, 2.5 eq.); (entry 2, 1.4g, 30 mmol, 5 eq.), (entry 3, 2.8g, 60 mmol, 10 eq.), (entry 4, 5.6g, 120 mmol, 20 eq.); reaction carried out in 25 mL three necked flask. [b] Determined by external eicosan gas chromatography calibration. [c] Two phases appear after complete addition of H_2O_2 [d] Conv. and sel. determinate after 2 hours reaction time.

An apparition of two liquid phases during H_2O_2 dropwise addition can explain this result. The same phenomenon was observed with 5 eq (table 6, entry 2). A larger quantity of formic acid (20 eq.) was also efficient after a shorter reaction time (2 hours) since conversion was similar to the reaction with 10 eq. after 4 hours reaction. In order to understand the role of this excess of formic acid, an additional experiment was accomplished with 5 eq. of formic acid in the presence of 2 mol% of TBAHS (tetrabutylammonium hydrogensulfate) which can act as a phase transfer agent. In these conditions, the conversion after 4 hours reached 75% with the selectivity in pelargonic and azelaic acid derivatives at 95% and 94% respectively.

Ketols can also be transformed by the Beckmann fragmentation of α -hydroxy oximes into nitrile and aldehyde.^{41,42} This transformation proceed in the presence of hydroxylamine. In addition in these conditions, aldehydes are converted into nitriles.⁴³ As a consequence, KA was mixed with 2.2 mol of hydroxylamine hydrochloride per mol of KA in methanol allowing the solubilisation of salts. These conditions were efficient since 47% of PN and 40% of MCO was obtained by GC. The methylated PA and AAM were also detected in 4 and 2% respectively.

Scheme 1. Formation of nitrile from KA.



The nature of the hydroxylamine is essential for the cleavage into nitrile since only the corresponding oxime of the KA is observed when the reaction was carried out with an aqueous solution of hydroxylamine. In order to observe the Beckmann fragmentation

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the presence of an acidic source is required as for example trifluoromethanesulfonic acid.⁴⁴

Conclusions

In conclusion, we have developed a two-step procedure for the oxidative cleavage of diols into carboxylic acids or nitriles. The first step can be performed according to two strategies. Both require the use of a heterogeneous nickel catalyst which could be recycled. The first one supposes a connection with vacuum and the second one needs an addition of a hydrogen scavenger, 1-decene. These procedures were mainly applied to fatty acid derivatives with success in order to obtain various hydroxyketones. The reactivity of these chemicals was also evaluated to reach carboxylic acids or nitriles in simple conditions.

Experimental Section

General procedure of dehydrogenation under vacuum: A schlenk, 100mL, equipped with condenser, and close with septum was purged 3 times with argon. DHSE, 2g, (6 mmol), 192 mg, 35 mol% of $^{64wt\%}Ni/SiO_2$ were introduced in the schlenk reactor. Atmosphere was purged by argon then hydrogen. The reaction was heated to 175 °C under hydrogen (balloon) during 15 min at 800 rpm (catalyst activation time). Schlenk tube was connected to the pump and pressure was controlled at 10 mbar. After 1 hour, the reaction was cooled down to room temperature and argon was introduced in the schlenk. The crude was diluted by 25 mL of ethyl acetate. Catalyst was filtered through celite and ethyl acetate was concentrated. The crude (1.90 g), was purified by silica column chromatography to afford 1.6 g (yield: 80%) of desired ketol compound (eluent: DCM/EtOAc = 100:0~98:2).

General procedure of dehydrogenation using 1-octene as hydrogen scavenger: A schlenk, 100 mL, equipped with condenser, and close with septum was purged 3 times with argon. DHSE, 2 g, (6 mmol), 192 mg, 35 mol% of $^{64wt\%}$ Ni/SiO₂ were introduced in the schlenk reactor. Atmosphere was purged again with argon and finally with hydrogen. The reaction was heated to 175 °C under hydrogen (balloon) during 15 min at 800 rpm (catalyst activation time). Thereafter, hydrogen atmosphere was replaced by argon. 924 mg of 1-decene (99%), 1.1 eq., was introduced dropwise by a syringe pump for 1 hour. After complete addition of 1-decene the reaction was introduced in the schlenk reactor. The crude was diluted by 25 mL of ethyl acetate. Nickel catalyst was filtered through celite and organic layers were concentrated. Decane is removed by fast distillation (60 °C: 0.5 mbar). The crude product 1.98 g, containing more than 90% of desired ketol compound was kept.

Acknowledgements

The authors thank the French National Agency for financial support through a Ph.D. grant to B.G. (ANR-13-CDII-0001-COUPOX).

Keywords: Dehydrogenation • diols • hydroxyketones • Nickel • Nitriles

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