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Organocatalytic Cleavage of Fatty 1,2-Diketones to Esters

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ABSTRACT. The cleavage of a fatty 1,2-diketone derived from methyl oleate into the corresponding esters, *i.e.*, methyl nonanoate and dimethyl azelate was studied by organocatalysis using oxygen as a clean oxidant. Only carbene generated from thiazolium salts and K₂CO₃ could efficiently catalyze this transformation. It was found that, under the optimized conditions, the oxidative cleavage leads to the formation of a 1:1 mixture of esters and potassium carboxylates. An acidic treatment of the mixture, followed by esterification with methanol, led to the desired

esters with 75 and 77% yield. This protocol was extended to a range of symmetrical and unsymmetrical fatty 1,2-diketones and the corresponding esters were isolated with 61-84% yield.

INTRODUCTION

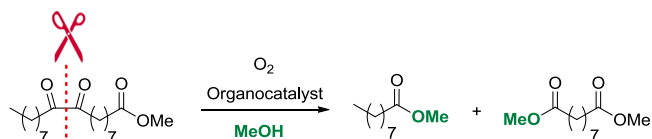
The development of new methodologies for the formation of carbon-carbon bonds has thoroughly occupied chemists during most of the last century, notably for increasing molecular complexity. In contrast, with the development of green and sustainable chemistry, the use of renewable resources is now often requiring the development of cleavage methods to produce chemicals with higher added-value.¹ Among the primary components of biomass, vegetable oils and fatty acid derivatives have attracted a lot of attention due to their wide availability, low cost and low toxicity.²⁻⁶ Unsaturated fatty compounds are particularly interesting since they can be cleaved to shorter fragments that could be used in the preparation of bio-based surfactants⁷⁻¹⁰ and polymers.^{11,12} Besides the specific thermal cracking of ricinoleic derivatives¹³⁻¹⁵ and the cross-metathesis with ethylene derivatives,¹⁶⁻¹⁹ most of the reported cleavage methods rely on the use of oxidants (oxidative cleavage). Therefore, they involve the formation of oxidized intermediates that are produced in-situ or prepared on purposes. The oxidative cleavage of ozonides, epoxides and 1,2-diols has been intensively studied,²⁰⁻²⁶ notably for the preparation of aldehydes, acids and esters. However, only very little attention has been devoted to fatty α -hydroxyketones²⁷⁻³⁴ and 1,2-diketones,³⁵⁻³⁷ even though these compounds are usually proposed as reaction intermediates.

In this context, we have recently reported the preparation of fatty α -hydroxyketones by either selective oxidation³⁸ or dehydrogenation of the corresponding fatty 1,2-diols.^{38,39} These α -hydroxyketones can be cleaved to the corresponding acids using H_2O_2 .³⁹ Alternatively, they can

be cleaved to aldehydes through a retro-benzoin process catalyzed by thiazolium salts under reactive distillation conditions.⁴⁰⁻⁴²

However, to the best of our knowledge, no example has been reported for the cleavage of fatty 1,2-diketones to the corresponding acids or esters. Actually, there are very few examples for the cleavage of 1,2-diketones (α -diketones). For instance, aromatic or aliphatic 1,2-diketones can be cleaved using bleach (10 equiv) to give the corresponding acids with good yields.⁴³ Moreover, it was also demonstrated that cyclic 1,2-diketones can also be cleaved to the corresponding esters using KHSO_5 (Oxone, 4 equiv) in methanol.⁴⁴ These two methods are relatively efficient but require the use of oxidants in large excess. Alternatively, catalytic methods were also developed for the cleavage of 1,2-diketones. In 1958, Kwart and Baevsky reported a kinetic study showing that the cyanide ion could catalyze the cleavage of aromatic diketones (benzils) into the corresponding aldehyde and ester.⁴⁵ This reaction was recently re-investigated by Sessler *et al.* in order to develop a selective cyanide indicator.⁴⁶ The authors showed that symmetrical benzil derivatives can be cleaved using tetrabutyl ammonium cyanide to give the corresponding aldehyde and ester in high yields. More recently, during the course of mechanism studies of the NHC-catalyzed oxidative esterification of aldehydes, Connon *et al.* showed that benzil was cleaved into aldehyde and ester in the presence of a triazolium precatalyst.⁴⁷ However, when the reaction was conducted in a mixture of THF/MeOH under anaerobic conditions (argon), methyl benzoate was only obtained with 50% yield. The same authors later reported the cleavage of cyclic aromatic 1,2-diketones to the corresponding diacids using similar conditions but under aerobic conditions (air) using a THF/ H_2O mixture.⁴⁸ The diacids were not isolated but further esterified using methyl iodide to give the diesters with good yields. However, when 1,2-cyclohexanedione was used, dimethyl adipate was only obtained with 18% yield, thus showing

the limitation of this method when aliphatic substrates are used as starting materials. In this context, we report here an efficient organocatalytic method for the cleavage of fatty 1,2-diketones to the corresponding esters using oxygen as a clean oxidant (Scheme 1).



Scheme 1. Organocatalytic cleavage of fatty 1,2-diketones to esters.

RESULTS AND DISCUSSION

Preparation of fatty 1,2-diketones

Three main methods have been described in the literature for the preparation of fatty 1,2-diketones. First, unsaturated fatty acids can be directly oxidized to 1,2-diketones using $KMnO_4$ under extremely diluted conditions (2 g.L^{-1}).³⁵ Second, they can be prepared from the corresponding epoxides using DMSO as an oxidant in the presence of $Bi(OTf)_3$.³⁶ Third, fatty 1,2-diols can be also oxidized to 1,2-diketones using NBS as an oxidant in the presence of pyridine in CCl_4 .³⁷ Although these methods give access to the desired products, they rely on toxic oxidants, thus leading to large quantities of waste. So, no clean (catalytic) oxidation method for the preparation of fatty 1,2-diketones has been reported to date. Considering that we have recently developed two green methods^{38,39} for the preparation of fatty α -hydroxyketones, we envisioned to use these key intermediates for the preparation of fatty 1,2-diketones.

The oxidation of the fatty α -hydroxyketone derived from methyl oleate to the corresponding 1,2-diketone was first investigated under metal-free conditions using DBU under air. Indeed, these conditions were reported to be efficient for the oxidation of benzoin to benzil,⁴⁹ and more recently, for the conversion of bio-based furoins to the corresponding α -diketones.⁵⁰ However, in our case, only 5% of the desired fatty diketone was obtained, probably due to the fact that aliphatic α -hydroxyketones are more difficult to oxidize than aromatic ones (*i.e.*, benzoin and furoins). Consequently, we have then focused our attention on a metal-based approach for the preparation of fatty 1,2-diketones.

Inspired from the work of Kirihaara,⁵¹ the α -hydroxyketones were oxidized using oxygen as a clean oxidant using VOCl_3 as a catalyst (1 mol%). The reaction was carried out in CH_3CN at room temperature for 18 hours (Figure 1).

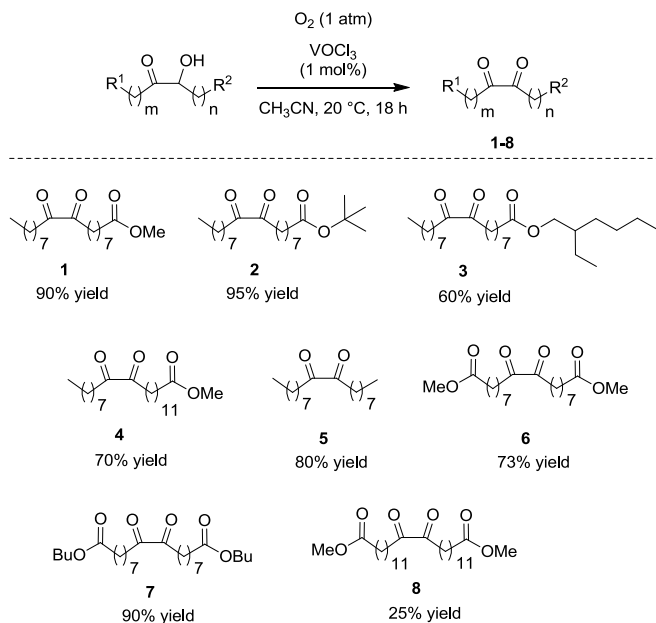


Figure 1. Preparation of fatty 1,2-diketones from α -hydroxyketones.

The reaction proceeded smoothly with unsymmetrical α -hydroxyketones (1:1 mixture of regioisomers) derived from methyl oleate, *tert*-butyl oleate, 2-ethylhexyl oleate and methyl erucate and the corresponding 1,2-diketones **1-4** were obtained with 60-95 % isolated yield. Similarly, symmetrical fatty α -hydroxyketone derivatives were also converted to the corresponding 1,2-diketones **5-7** with high yields (73-90%). However, fatty diketone **8** was only obtained with 25% yield due to the low solubility of the starting material under the conditions used.

Cleavage of fatty 1,2-diketones to esters

With a range of fatty 1,2-diketones in hands, their organocatalytic cleavage to esters was first investigated using diketone **1** as a model substrate. The reaction was first carried out under air (1 atm) in the presence of thiazolium precatalyst **9** (20 mol%) and K_2CO_3 (20 mol%) in MeOH at 65°C (Table 1).⁵²

Table 1. Influence of atmospheric conditions for cleavage of diketone.^a

Reaction scheme: Diketone **1** + Thiazolium precatalyst **9** (20 mol%) + K_2CO_3 (20 mol%) in MeOH, 65°C, 3 h → Ester **10** + Ester **11**.

Entry	Atmosphere	Conv. ^b (%)	Yield ^b (%)	Yield ^b (%)
1	Air	99	33	25
2	O ₂	99	35	33
3	Argon	15	-	-

^a Reaction conditions: 25-mL Schlenk flask, diketone **1** (0.5 mmol), thiazolium salt **9** (20 mol%), K₂CO₃ (20 mol%), MeOH (0.5M), 65°C, 3 h. ^b Conversion and yield of products were determined by GC using *n*-hexanadecane as an internal standard. ^c 100 mol% of K₂CO₃ was used.

Under these conditions, methyl pelargonate **10** and dimethyl azelate **11** were obtained with 33 and 25% yield, respectively (Table 1, entry 1). When the reaction was conducted under oxygen, the yields slightly increased to 35 and 33% (Table 1, entry 2). These moderate yields could be explained by the formation of two heavier products **12** and **13** that could be observed in the GC chromatogram (Figure 2).

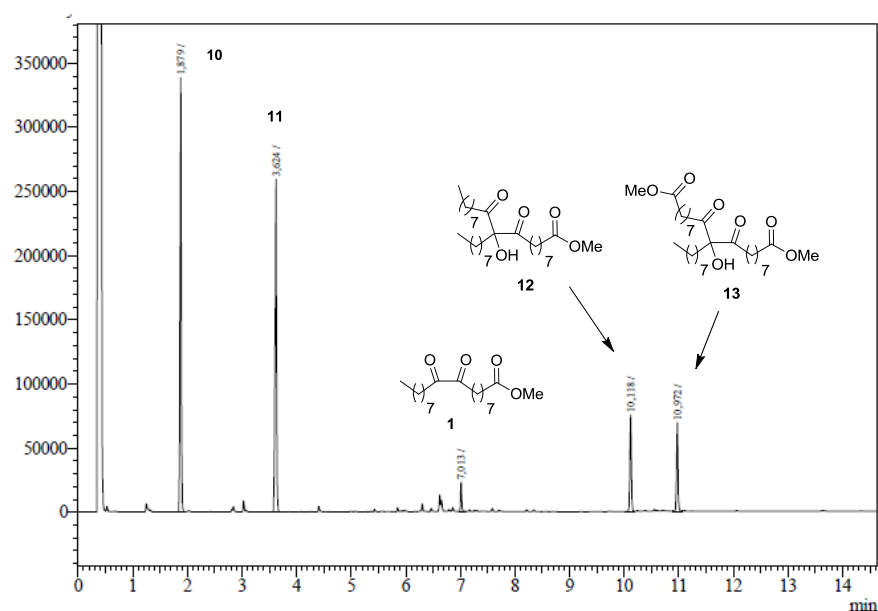


Figure 2. GC chromatogram of the oxidative cleavage of 1,2-diketone **1** (from Table 1, entry 1).

In fact, the formation of these by-products could be explained from a mechanism point of view (Figure 3).

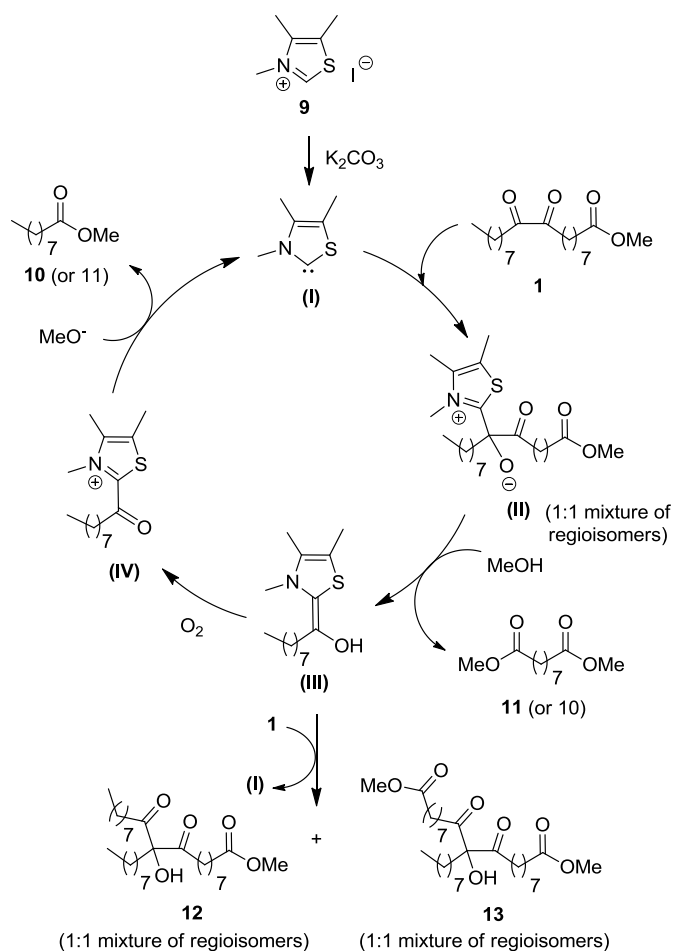
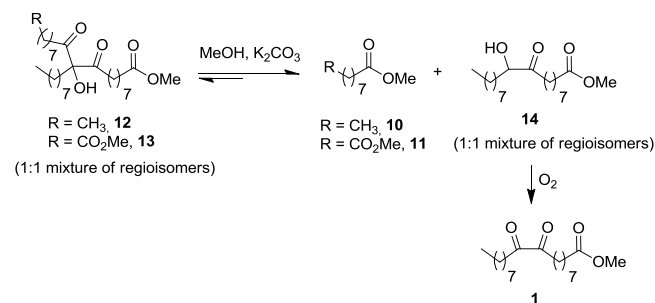


Figure 3. Proposed mechanism for the cleavage of 1,2-diketones to esters and formation of the byproduct (only one regioisomer is represented for clarity).

First, thiazolium **9** is deprotonated in the presence of K_2CO_3 to generate the active thiazolyliene species **(I)**. The free carbene could undergo nucleophilic addition onto diketone **1** to form intermediate **(II)** as 1:1: mixture of regioisomers. This species could be cleaved in the presence of methanol to give a first ester and Breslow intermediate **(III)**. Then, there are two possible pathways from this key intermediate. On the one hand, the Breslow intermediate could be oxidized in the presence of oxygen to form the acyl thiazolium species **(IV)**, following by nucleophilic addition of methoxide to liberate a second ester and the free carbene. This first pathway is thus involved in the formation of the desired esters **10** and **11**. On the other hand, the

The formation of such compounds was previously demonstrated by Massi *et al.* who showed that α -diketones could be used as acyl anion equivalents to give α -hydroxy 1,3-diketones in the presence of a thiamine-based catalyst.⁵³ However, the formation of these α -hydroxy 1,3-diketones is only predominant when the reaction is conducted without any oxidant. This is in accordance with our results obtained when the reaction was carried out under argon atmosphere (Table 1, entry 3). Indeed, under these conditions, the conversion reached 15% and only byproducts **12** and **13** were observed (esters **10** and **11** were not detected). In order to improve the results, the formation of such compounds should be avoided. According to Connon *et al.*, α -hydroxy 1,3-diketones could be cleaved to ester and α -hydroxyketone in the presence of MeOH and base, through the formation of a hemi-ketal.⁴⁷ In our case, compounds **12** and **13** could produce esters **10** and **11** and the corresponding α -hydroxyketone **14** could be further oxidized to regenerate 1,2-diketone **1** (Scheme 2).



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So, in order to promote this reverse reaction, the reaction was carried out under oxygen but with an excess of K_2CO_3 (100 mol%) (Table 1, entry 4). Satisfyingly, the yield of esters **10** and **11** increased to 38 and 39%, respectively, and no trace of byproducts **12** and **13** was observed by GC. Consequently, these conditions were selected for further optimization.

A range of commercially available azolium salts was next screened as precatalysts for the oxidative cleavage of 1,2-diketone **1** under typical conditions (20 mol% of azolium salt, 100 mol% of K_2CO_3) (Table 2).

Table 2. Screening of precatalysts for the oxidative cleavage of diketone.^a

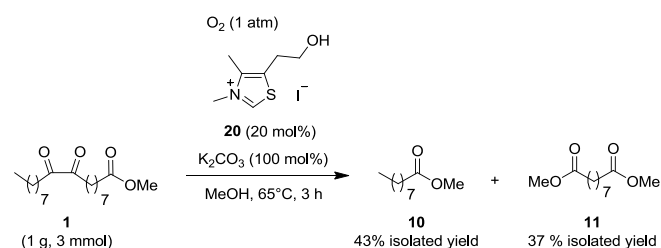
O_2 (1 atm)
azolium salt (20 mol%)
 K_2CO_3 (100 mol%)
MeOH, 65°C, 3 h

Entry	NHC precatalyst	Conv. ^b (%)	Yield ^b (%)	Yield ^b (%)
1	 15	99	7	11
2	 16	99	6	3
3	 17	99	6	5
4	 18	98	7	6
5	 9	98	38	39
6	 19	94	39	31
7		99	42	42
8 ^c	 20	99	17	13
9 ^d		99	12	15
10	 21	99	40	36

^a Reaction conditions: 25-mL Schlenk flask, diketone **1** (0.5 mmol), azolium salt (20 mol%), K_2CO_3 (100 mol%), MeOH (0.5 M), 65°C, 3 h. ^b Conversion and yield of products were determined by GC using *n*-hexanadecane as an internal standard. ^c 200 mol% of K_2CO_3 . [d] 300 mol% of K_2CO_3 .

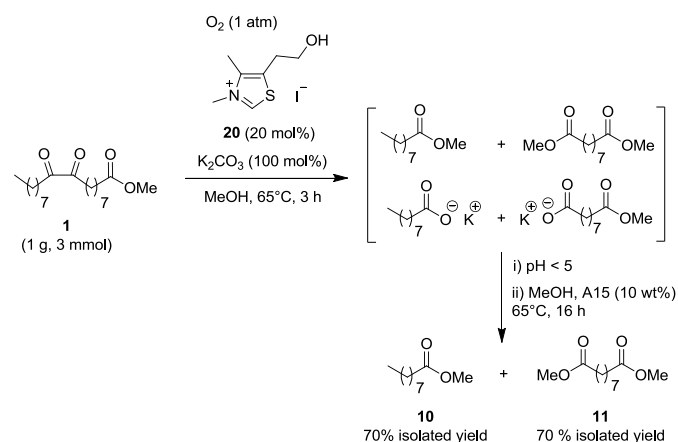
Triazolium **15**, imidazolium **16** and benzothiazolium salts **17-18** were first investigated and they all gave a full conversion (Table 2, entries 1-4). However, none of these catalysts could generate the desired esters with significant yields. In these cases, the heavy byproducts **12** and **13** were formed along with other unidentified heavier byproducts. The presence of aldehydes (nonanal and methyl 9-oxononanoate) was also observed by GC and their corresponding acids were also detected by mass spectroscopy (ESI, negative mode). However, the amount of the byproducts was not quantified at this stage of the study. On the contrary, only thiazolium salts **9**, **19-21** could efficiently catalyze the cleavage of 1,2-diketone **1** (Table 2, entries 5-10). The best results were obtained with thiamine-based catalyst **20**, providing a quantitative conversion and 42% yield of two esters **10** and **11** (Table 2, entry 7). Increasing the amount of K₂CO₃ or using other bases (see ESI) did not allow to improve the results (Table 2, entries 8-9). Considering that thiazolium **20** has a free hydroxy group that could be potentially oxidized during the process, thiazolium salt **21**, bearing a *O*-methyl protection, was synthesized and evaluated under the same conditions (Table 2, entry 10). No better results were obtained with this catalyst, showing that oxidation of the OH group in thiazolium **20** does not occur, or if so, it has a negligible impact on the reactivity. Finally, a control experiment was also carried out using only 100 mol% of K₂CO₃. Under these conditions, esters **10** and **11** can be still detected but the reaction mixture was very messy (see GC chromatogram in ESI), indicating the crucial role of the thiazolium precatalyst **20** to promote the desired reaction.

After optimization, the conversion was complete and the maximum yield for each ester reached a plateau at 42%. To confirm this result, the reaction was scaled-up using 1 g of 1,2-diketone **1** derived from methyl oleate. Using thiazolium salt **20**, the isolated yield of **10** and **11** reached 43 and 37%, respectively, thus confirming the previous results obtained by GC titration (Scheme 3).



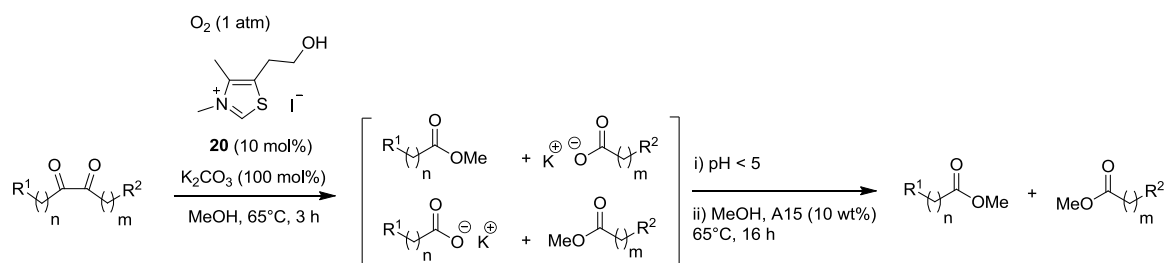
Scheme 3. Scale-up reaction for the oxidative cleavage of 1,2-diketone **1** to esters.

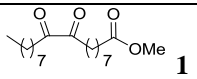
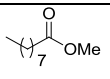
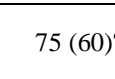
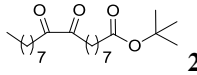
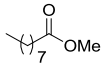

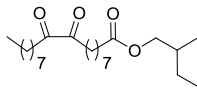
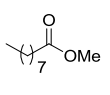

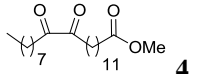
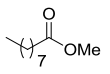

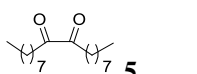
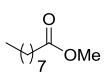
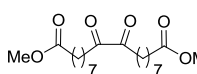

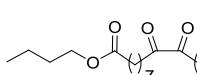



Based on this scale-up reaction and our previous observations, other species, representing about half of the cleavage, must be generated during the reaction. However, these species were neither detected by GC nor isolated by column chromatography. Moreover, it should be noted that an excess of the base is required to afford the highest yield of esters. So, we hypothesized that the corresponding potassium carboxylates were also formed as co-products. To evaluate this hypothesis, the cleavage reaction of 1,2-diketone **1** was carried out under optimized conditions but the work-up was modified (Scheme 4).



Scheme 4. Scale-up reaction for the oxidative cleavage of 1,2-diketone **1** to esters.

An acid treatment was applied until $\text{pH} < 5$ to release the free acids and the formation of these species was confirmed by GC (see ESI). The esterification of the mixture in methanol in the presence of Amberlyst-15 gave esters **10** and **11** as the only products as also confirmed by GC (see ESI). Finally, the products were purified by column chromatography to give esters **10** and **11** with 70% isolated yield. This result clearly indicate the formation of potassium carboxylates as reaction intermediates. Moreover, they have been detected by negative mode ESI mass spectroscopy (see ESI). The substrate scope was then investigated using a catalyst loading of 10 mol%⁵⁴ and using an acidification/esterification work-up (Table 3).

Table 3. Scope for the cleavage of fatty 1,2-diketones to esters.^a

Entry	Fatty 1,2-diketones	Conv. ^[b] (%)	1 st ester	Isolated yield (%)	2 nd ester	Isolated yield (%)
1	 1	98 (98) ^c	 10	75 (60) ^c	 11	75 (60) ^c
2	 2	98	 10	68	 11	74
3	 3	99	 10	75	 11	70
4	 4	99	 10	67	 22	73
5	 5	99	 10	68	-	-
6	 6	99	-	-	 11	84
7	 7	99	-	-	 11	61
8	 8	99	-	-	 22	74

^a Reaction conditions: 25-mL Schlenk flask, diketone (0.5 mmol), thiazolium salt **20** (10 mol%), K₂CO₃ (100 mol%), MeOH (0.5M), 65°C, 3 h. ^b Conversion was determined by GC. ^c Results for the scale-up reaction using 5 mmol of diketone.

Unsymmetrical fatty 1,2-diketones were first considered. Diketone **1** gave 75% of methyl pelargonate **10** and 77% of dimethyl azelate **11**, thus showing that decreasing the catalyst loading to 10 mol% has little impact on the results (Table 3, entry 1). However, lower yields (60%) were obtained for a scale-up reaction using a 10-fold amount of starting material (Table 3, entry 1, results in brackets). The same esters **10** and **11** were also isolated with 68 and 74% yield, from diketone **2** derived from *tert*-butyl oleate (Table 3, entry 2). This result shows that *tert*-butyl ester intermediates underwent transesterification in the presence of methanol and Amberlyst 15 to give the corresponding methyl esters. The same phenomenon also occurs using diketone **3** as a starting material and esters **10** and **11** were obtained with 73 and 70% yields (Table 3, entry 3). Diketone **4**, derived from methyl erucate, gave ester **10** and dimethyl brassylate **22** with 68 and 74% yield, respectively (Table 3, entry 4). Symmetrical fatty 1,2-diketones were next considered and they all gave satisfying yields. Diketone **5** gave methyl pelargonate **10** as unique product with 67% yield (Table 3, entry 5). Symmetrical diketones **6** and **7** gave dimethyl azelate **11** with 84 and 61% yield, respectively after (trans)esterification with methanol (Table 3, entries 6-7). Finally, diketone **8** afforded dimethyl brassylate **22** as the sole product with 74% yield (Table 3, entry 8). The monoesters could find applications in the preparation of biobased surfactants while the diesters could be used as monomers for the synthesis of renewable polyesters.

CONCLUSIONS

In conclusion, we have demonstrated that fatty 1,2-diketones can be efficiently cleaved to the corresponding esters using oxygen as a clean oxidant. The reaction occurs in methanol in the presence of a thiazolium precatalyst and K_2CO_3 and generates a 1:1 mixture of methyl esters and

potassium carboxylates. An acidic treatment of the mixture, followed by (trans)esterification with methanol, led to the desired methyl esters with good isolated yields. The optimized conditions were applied to a range of symmetrical and unsymmetrical fatty 1,2-diketones and the corresponding esters were isolated with 61-84% yield. The conditions developed in this work highlight that aliphatic (enolizable) 1,2-diketones can be cleaved with similar efficiency that aromatic 1,2-diketones (benzils).

EXPERIMENTAL

General procedure for the oxidation of fatty α -hydroxyketones to 1,2-diketones. Following a modified reported procedure,⁵¹ in a 250-mL two-neck flask, the α -hydroxyketone (1 equiv) was suspended in MeCN and VOCl_3 (1 mol%) in MeCN was added dropwise over 15 minutes. The flask was equipped with an oxygen balloon and the yellow suspension was stirred at room temperature for 24 hours (the reaction was followed by GC and the completion was indicated by a green color of the reaction mixture). The reaction mixture was quenched by a saturated NaHCO_3 solution (twice) and extracted with a mixture of heptane/EtOAc (1:1). The organic layer was washed with saturated NH_4Cl solution (twice), saturated NaCl solution (twice), dried (MgSO_4), filtered and the filtrate was evaporated under reduced pressure to give the crude product. The residue was purified by column chromatography (cyclohexane/ethyl acetate 100:0 to 95:5) or by recrystallization in ethanol.

General procedure for the organocatalytic cleavage of fatty 1,2-diketones to esters. In a 25-mL round bottom flask, a 1,2-diketone (1 equiv), a NHC precatalyst (10 mol%) and K_2CO_3 (1 equiv) were introduced under oxygen atmosphere (balloon), then MeOH was added. The reaction mixture was heated at 65°C for 3 hours. After cooling to room temperature, the mixture is filtered on sintered glass and HCl (3M in MeOH) was added to reach a pH around 1. Then, 10wt % of Amberlyst 15 (acidic resin) was added and the reaction is left overnight under stirring in MeOH at 65°C. The solution is filtered through sintered glass and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (cyclohexane / ethyl acetate: 100:0 to 96:4).

ASSOCIATED CONTENT

Supporting Information. The supporting information contains the general procedures, the characterization data of fatty 1,2-diketones and esters, as well as 1H and ^{13}C NMR spectra of all compounds.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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- 54 See supporting information for the optimization of the catalyst loading.

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“Organocatalytic scissors” were used to cleave fatty 1,2-diketones to esters using oxygen as a clean oxidant.

