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Thiazolylidene-Catalysed Cleavage of Methyl Oleate-Derived α -Hydroxyketone to the Corresponding Free Aldehydes

Elsa Deruer, Nicolas Duguet* and Marc Lemaire*

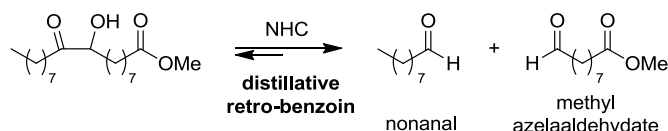
Abstract: Thiazolylidene-catalysed cleavage of the α -hydroxyketone derived from methyl oleate gave the corresponding aldehydes under non-oxidative conditions through a retro-benzoin process. The aldehydes produced are in equilibrium with their corresponding acyloins. To illustrate the synthetic utility of this protocol, the aldehydes were recovered by distillation.

Among the primary components of biomass, triglycerides (vegetable oils and animal fats) are of great interest since they exhibit low oxygen content contrary to carbohydrates and lignin. Consequently, they could be readily transformed into biofuels,^[1] platform chemicals^[2] and biopolymers.^[3] Methyl oleate produced by methanolysis of vegetable oils is probably one the most interesting starting material due to the presence of a single internal double bond. First, the double bond could be functionalized to epoxide,^[4] diol,^[5] mono- or diketone,^[6] among others and these intermediates could be used as such or further transformed. The C=C bond could be also cleaved to give shorter fragments such as C9-acids or aldehydes through oxidative^[7] or reductive^[8] ozonolysis, respectively. The double bond of methyl oleate is also a suitable site for metathesis reactions. For example, methyl oleate could undergo cross-metathesis with ethylene (ethenolysis) to give C10-compounds with a terminal double bond that could be further transformed.^[9] Moreover, methyl oleate could undergo self-metathesis to give C18-compounds that could be of great interest for the polymer or the biofuel industry.^[10] A saturated C19-diester could also be prepared through isomerization of the internal double bond to the terminal position where it is transformed to the corresponding methyl ester by methoxycarbonylation.^[11] Among all these transformations, the reductive ozonolysis is the only direct route providing fatty aldehydes which are of great interest for various applications. For example, nonanal could be used as such or for the preparation of 100% bio-based surfactants through the reductive alkylation of polyols.^[12] Methyl azelaaldehyde could be transformed to monomers for the preparation of polyesters and polyamides through reduction or reductive amination, respectively.^[8] However, albeit excellent atom-economies, this method requires the use of ozone (O₃)

which is highly toxic and explosive. In this context, alternatives to prepare these bio-based fatty aldehydes will be of great interest.

The utilization of renewable feedstocks has recently boosted the use of organocatalysts for biorefining.^[13] In this context, *N*-Heterocyclic Carbenes (NHCs) have been particularly found suitable for the upgrading of biomass-derived furan aldehydes, such as furfural and 5-hydroxymethylfurfural (HMF),^[14] through the well-established benzoin condensation. This strategy has also been applied for the upgrading of bioethanol-based acetaldehyde to acetoin.^[15] The (asymmetric) benzoin condensation has been extensively studied^[16] and its reversibility has been demonstrated in some occasions.^[17,18] It has also been recognized that this retro-benzoin process occurs in a biochemical reaction - catalysed by Vitamin B1 (Thiamine) - in the transketolase (TK) enzyme involved in the metabolism of carbohydrates.^[19] However, this reversibility has been underexploited^[20] and examples of its synthetic utility are scarce. Miyashita *et al.* have first reported that ketones could be produced from α -substituted benzoin using cyanide ion or a range of NHCs as catalysts, exploiting the fact that ketones are usually more stable than aldehydes.^[21] More recently, Chi *et al.* have elegantly shown that formaldehyde equivalents could be generated from carbohydrates through a retro-benzoin process catalysed by a thiazolium salt.^[22] This very reactive one-carbon acyl anion was trapped by enones to give β -formylketones, taking advantage of the irreversible character of the Stetter reaction. Although these two methodologies give access to the retro-benzoin products, they do not allow the isolation of the free aldehydes.

In the context of the valorization of vegetable oils, we envisioned that retro-benzoin condensation of methyl oleate-derived α -hydroxyketone (methyl 9-hydroxy-10-oxostearate) would produce the corresponding aldehydes, *i.e.*, nonanal and methyl azelaaldehyde (Scheme 1). We also hypothesized that removing the products from the reaction mixture by distillation would shift the equilibrium towards their formation. Herein, we report, to the best of our knowledge, the first retro-benzoin method that allows the generation and the isolation of aliphatic free aldehydes from renewable resources.



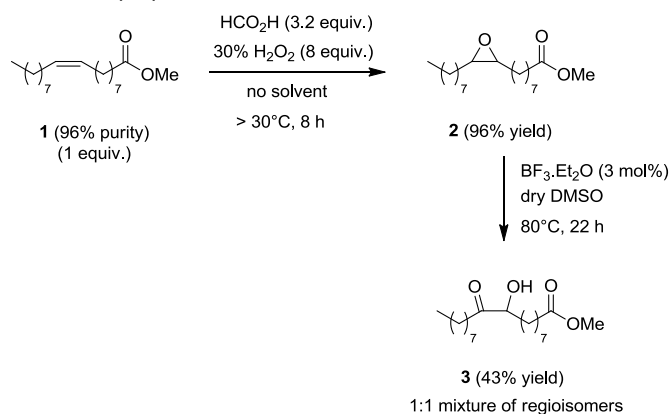
Scheme 1. NHC-catalysed distillative retro-benzoin condensation of methyl oleate-derived α -hydroxyketone (methyl 9-hydroxy-10-oxostearate).

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In order to test our hypothesis, the α -hydroxyketone of methyl oleate was prepared from commercially available methyl oleate

in a two-step sequence involving epoxide formation and subsequent oxidative ring-opening (Scheme 2). First, methyl oleate **1** (96% purity) was converted to methyl 9,10-epoxystearate **2** with 96% isolated yield according to the procedure reported by Doll *et al.*^[6] Then, the epoxide underwent oxidative ring-opening by DMSO following the procedure of Brousse and Lefort^[23] to give the desired α -hydroxyketone **3** as a 1:1 mixture of regioisomers with 43% isolated yield after flash chromatography. The unreacted starting material **2** has also been recovered with 41% isolated yield. It should be noted that even if the original procedure has not been optimized,^[24] it allows the preparation of sufficient material for our studies.



Scheme 2. Preparation of methyl oleate-derived α -hydroxyketone.

In an initial attempt, α -hydroxyketone **3** was heated at 130°C for 24 hours in the presence of commercially available thiazolium salt **4** (20 mol%) and K_2CO_3 (20 mol%). The 1H NMR spectrum of the crude reaction mixture revealed the formation of the desired aldehydes **5** and **6** (10% yield based on the conversion of α -hydroxyketone **3**), thus validating our approach that α -hydroxyketone could be cleaved under non-oxidative conditions. Encouraged by this preliminary result, we quickly turned our attention to the use of microwave activation. Under these conditions, the conversion reached 24% after only 30 minutes and the desired aldehydes **5** and **6** were obtained with 19% yield along with 5% of the symmetric acyloins **7** and **8** (Table 1, entry 1).^[25] We hypothesized that these products were formed by thiazolium-catalysed self-benzoin condensation of the previously generated aldehydes **5** and **6** and that the whole system is an equilibrium. Interestingly, by analogy with the olefin self-metathesis of methyl oleate, acyloins **7** and **8** could be seen as the benzoin self-metathesis products of α -hydroxyketone **3**. Other commercially available azolium salts **9–15** were next screened as pre-catalysts. Thiamine-derived thiazolium salt **9** was also found active but the aldehydes were formed with a slightly lower yield (14%) and almost no acyloins were produced (Table 1, entry 2). Surprisingly, NHCs derived from structurally-related benzothiazolium salts **10** and **11** were almost inactive (Table 1, entries 3–4). Other pre-catalysts such as imidazolium **12**, imidazolinium **13** and triazolium salts **14** and **15** were also screened and, similarly, none of these species could efficiently lead to the formation of the cleavage products (Table 1, entries 5–8). Finally, only thiazolium-based catalysts **4** and **9** have been

found sufficiently active for this transformation. These results corroborate the findings of Chi who has also proved the superiority of thiazolium salts to catalyze the retro-benzoin of carbohydrate derivatives.^[22]

Table 1. Azolium pre-catalysts screening.^[a]

Entry	Azolium salt	Conv [%]	Yield [%]			
			5	6	7	8
1	4	24	19	19	5	5
2	9	16	14	14	2	2
3	10	2	2	2	0	0
4	11	2	2	2	0	0
5	12	2	2	2	0	0
6	13	0	0	0	0	0
7	14	0	0	0	0	0
8	15	3	3	3	0	0

[a] Conditions: Microwave tube, α -hydroxyketone **3** (1:1 mixture of regioisomers, 0.2 mmol), azolium salt (20 mol%), K_2CO_3 (20 mol%), dry CH_3CN (2 mL), 130°C, 30 min. Conversion and yields were determined by GC using hexadecane as internal standard.

The influence of the base was next probed using thiazolium **4** at 150°C under microwave irradiation (Table 2). Among the organic bases tested, Et_3N and iPr_2NEt gave poor results (Table 2, entries 1–2). When using a range of carbonates, the conversion of α -hydroxyketone **3** gradually increased from 2% with Li_2CO_3 to 39% with K_2CO_3 (Table 2, entries 3–5). However, these results could not be improved using other carbonates such as Rb_2CO_3 and Cs_2CO_3 (Table 2, entries 6–7). Other potassium bases such as $KHCO_3$, $KOAc$ and KOH were also found effective to promote the reaction but to a lesser extent compared to K_2CO_3 (Table 2, entries 8–10). The effect of the catalyst loading was then probed. Predictably, decreasing the loading of both thiazolium **4** and

K_2CO_3 from 20 to 5 mol% led to a moderate drop of conversion from 39 to 23% (Table 2, entries 5, 11-12). Interestingly, the selectivity of aldehydes **5** and **6** was higher (82%) when using 5 and 10 mol% of the NHC than with 20 mol% (72%). This property could be advantageously used for the selective recovery of aldehydes by distillation. The reaction was also carried out with 20 mol% of precatalyst **4** and 10 mol% of K_2CO_3 but neither the conversion of **3** nor the selectivity of aldehydes were improved under these conditions (Table 2, entry 13). In order to find the equilibrium of this system, the reaction was

carried out at higher temperature. At 170°C under microwave irradiation, the conversion reached 56 and 60% after 30 and 60 minutes, respectively (Table 2, entries 14-15). Under these conditions, aldehydes **5** and **6** were formed with 40% yield, respectively, and acyloins **7** and **8** with 20% yield, respectively. These results could not be improved after a prolonged time indicating that equilibrium was probably reached. Satisfyingly, the reaction mixture was relatively clean indicating that few side-reactions occurred under these optimized conditions (Figure 1).

Table 2. Screening of bases and reaction parameters.^[a]

Entry	4 [mol%]	Base	Base [mol%]	Conv. [%]	Yields [GC, %]			
					5	6	7	8
1	20	Et ₃ N	20	7	7	7	0	0
2	20	iPr ₂ NEt	20	7	7	7	0	0
3	20	Li ₂ CO ₃	20	2	2	2	0	0
4	20	Na ₂ CO ₃	20	13	13	13	0	0
5	20	K ₂ CO ₃	20	39	28	28	11	11
6	20	Rb ₂ CO ₃	20	30	24	24	6	6
7	20	Cs ₂ CO ₃	20	30	16	16	14	14
8	20	KHCO ₃	20	29	23	23	6	6
9	20	KOAc	20	32	24	24	8	8
10	20	KOH	20	35	27	27	8	8
11	10	K ₂ CO ₃	10	33	27	27	6	6
12	5	K ₂ CO ₃	5	23	19	19	4	4
13	20	K ₂ CO ₃	10	32	23	23	8	8
14 ^[b]	20	K ₂ CO ₃	20	56	40	40	16	16
15 ^[c]	20	K ₂ CO ₃	20	60	40	40	20	20
16	20	-	-	0	0	0	0	0
17	-	K ₂ CO ₃	20	0	0	0	0	0
18	-	-	-	0	0	0	0	0

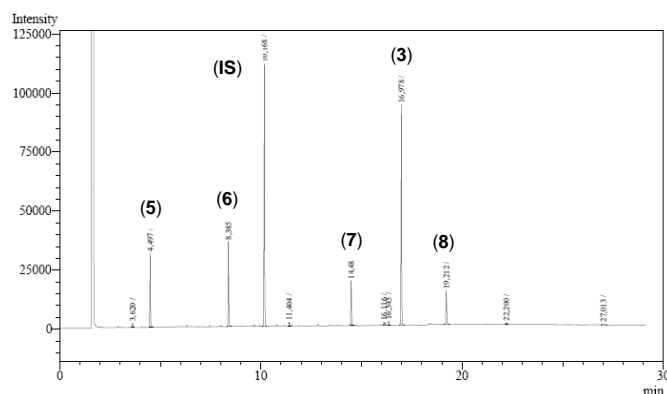
[a] Conditions: Microwave tube, α -hydroxyketone **3** (1:1 mixture of regioisomers, 0.2 mmol), thiazolium **4**, base, dry CH₃CN (2 mL), 150°C, 30 min. Yields were determined by GC using hexadecane as internal standard and refer to the conversion of α -hydroxyketone **3**. [b] 170°C, 30 min. [c] 170°C, 60 min.

Finally, control experiments have been carried out to verify that NHC derived from **4** is the active catalytic species. Addition of α -hydroxyketone **3** to either thiazolium pre-catalyst **4** (20 mol%) or K_2CO_3 (20 mol%) gave no conversion to the corresponding

aldehydes (Table 2, entries 16-17). Moreover, heating α -hydroxyketone **3** in CH₃CN under microwave irradiation also returned exclusively the starting material (Table 2, entry 18). These control experiments confirm that thiazolylidene species

generated from **4** is responsible for the catalytic cleavage of the α -hydroxyketone derived from methyl oleate.

Figure 1. GC chromatogram of the crude reaction mixture after 60 min. at 170°C. IS = Internal standard (hexadecane).



From these results, the following mechanism could be proposed (Figure 2). First, thiazolium salt **4** could be deprotonated with K_2CO_3 to generate thiazolidene **I** as the active catalyst. Addition of thiazolidene **I** to α -hydroxyketone **3** (1:1 mixture of regioisomers) would lead to intermediate **II**. Then, proton transfer from **II** to **III** would produce Breslow intermediate **IV** with concomitant exclusion of aldehyde **6** (or **5** with the other regioisomer). Finally, further proton transfer would generate intermediate **V** that would release aldehyde **5** (or **6** starting from the other regioisomer) and thiazolidene active catalyst **I**. As the reaction is reversible, aldehydes **5** or **6** could re-enter the catalytic cycle to produce a Breslow intermediate that would react with a second aldehyde to finally produce symmetrical α -hydroxyketones **7** and **8**. The fact that this retro-benzoin process could only be efficiently catalyzed by thiazolium precursors could be attributed by the relative stability of the Breslow intermediate. Indeed, Holl  czki and Nyul  szki have

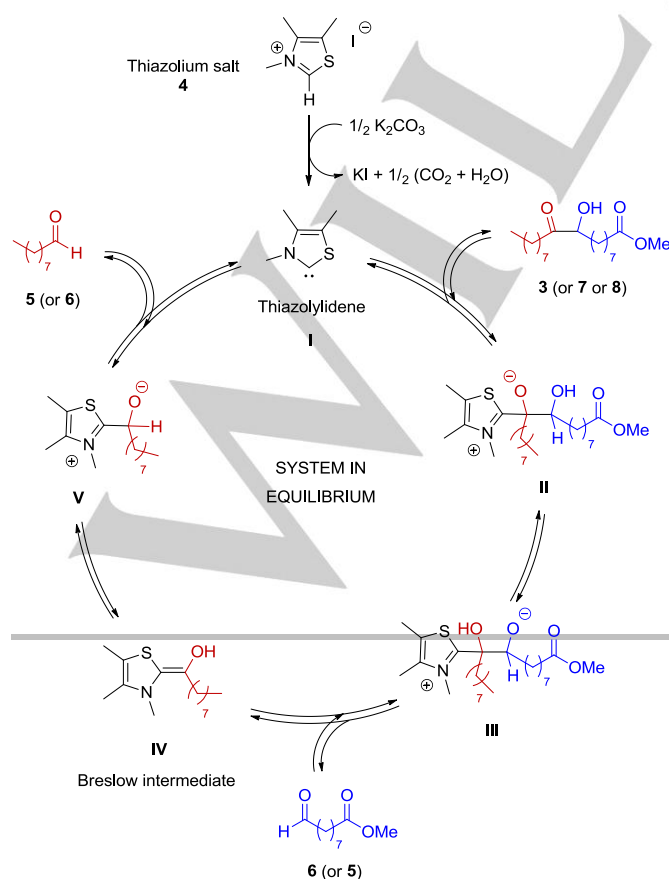
recently shown that the Breslow intermediate generated from thiazol-2-ylidene was found more stable (by ca. 10 kcal/mol) than those produced from other NHC precursors such as imidazolium and triazolium salts, thus increasing the reversibility of the reaction.^[27]

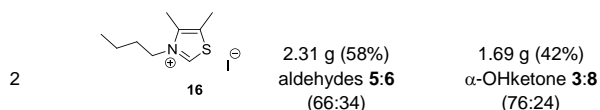
Figure 2. Mechanism proposal (only one regioisomer of **3** is represented).

In order to prove the synthetic utility of this method, we envisioned that removing aldehydes **5** and **6** from the reaction mixture by distillation would shift the equilibrium towards their formation and would also limit the formation of acyloins **7** and **8**. In order to avoid the formation of potential aldol by-products, the pre-generation of the NHC was favored and the aldehydes were simultaneously distilled. Neat α -hydroxyketone **3** (4.00 g) was heated at 180°C (oil bath) in the presence of 10 mol% of the thiazolidene active species [(pre-generated from thiazolium salt **4** (10 mol%) and K_2CO_3 (10 mol%)]]. The distillate was collected from 58 to 91°C under reduced pressure (4–6 mbar). After 3 hours, 1.42 g (36 m% yield) of aldehydes **5** and **6** was recovered (Table 3, entry 1) as a 63:37 mixture as determined by GC analysis. Encouragingly, the residue showed no significant sign of degradation and only starting material **3** and acyloin **8** were recovered. However, we noticed that pre-catalyst **4** was slightly degraded to 4,5-dimethylthiazole resulting in a low yield. Therefore, thiazolium **16** showing an ionic liquid-like structure was specifically designed to prevent the degradation. Satisfyingly, under these conditions, aldehydes **5** and **6** were recovered as a 66:34 mixture with an improved 58% global yield (Table 3, entry 2). In that case, the residue showed a significant proportion (24%) of acyloin **8**. Further addition of freshly pre-generated catalyst (10 mol%) to the residue did not improve the yield of aldehydes. This indicates that the conversion was limited due to the lack of material in the distillation set-up rather than resulting from catalyst deactivation, thus encouraging the development of a continuous distillation process.

Table 3. Recovery of aldehydes by distillation.^[a]

Entry	Thiazolium salt	Distillate composition	Residue composition
1		1.42 g (36%) aldehydes 5:6 (63:37)	2.58 g (64%) α -OHketone 3:8 (95:5)





[a] Conditions: distillation set-up, pre-generation of catalyst from thiazolium salt (10 mol%), K_2CO_3 (10 mol%), dry CH_3CN (4 mL) for 10 minutes at RT. Removal of K_2CO_3 and evaporation of CH_3CN . Then, α -hydroxyketone **3** (1:1 mixture of regioisomers, 4.00 g), 180°C, 4–6 mbar, 3 hours.

In conclusion, we have demonstrated that the α -hydroxyketone derived from methyl oleate could be cleaved under non-oxidative conditions to give the corresponding aldehydes, *i.e.*, nonanal **5** and methyl azelaaldehyde **6**. The reaction proceeds through a retro-benzoin process that is specifically catalyzed by a thiazolylidene species. It has been shown that the aldehydes are in equilibrium with their corresponding acyloins **7** and **8**, which could be considered as the benzoin self-metathesis products of α -hydroxyketone **3**. In order to illustrate the synthetic utility of this method, the cleavage products were removed by distillation, thus shifting the equilibrium towards the formation of the desired aldehydes. Current studies are now focused upon improving the access to α -hydroxyketone starting material and optimizing the structure of the catalyst. Further investigations will also focus on the development of a continuous distillation process.

Experimental Section

Procedure for the preparation of methyl 9,10-epoxystearate (2): Following a modified literature procedure,⁶ in a 50-mL round-bottom three-necked flask, methyl oleate **1** (Alfa Aesar, 96 %) (10 mL, 29.4 mmol, 1 equiv) was introduced with formic acid (3.6 mL, 94.1 mmol, 3.2 equiv). Hydrogen peroxide (7 mL, 234 mmol, 8 equiv) was added dropwise over a 15-min period, thanks to a dropping funnel and an ice bath was used to control the exothermicity. Then, the mixture was magnetically stirred at room temperature for 8 h. The reaction was followed by GC. The temperature should not exceed 30°C. The organic layer was extracted with heptane (10 mL), neutralized with a saturated $NaHCO_3$ solution (5x10 mL), washed with H_2O (3x10 mL) and a saturated $NaCl$ solution (2x5 mL). The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure to give the title compound **2** (8.80 g, 96 %) as a colorless liquid. 1H NMR (300 MHz, $CDCl_3$): δ_H = 0.86 (t, 3H, J =6.5), 1.10–1.52 (m, 24H), 1.52–1.70 (m, 2H), 2.28 (t, 2H, J =7.4), 2.80–2.96 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 14.2 (CH_3), 22.8, 25.0, 26.6, 26.7, 27.90, 27.94, 29.1, 29.29, 29.33, 29.4, 29.6, 29.7, 32.0 (13 CH_2), 34.2 (CH_2), 51.5 (CH_3), 57.28 (CH), 57.33 (CH), 174.3 (C). See supporting information for full characterization.

Procedure for the preparation of methyl 9(10)-hydroxy-10(9)-oxostearate (3): Following a literature procedure,²³ in a 25-mL round bottom flask, under an argon atmosphere, methyl 9,10-epoxystearate **2** (1.00 g, 3.2 mmol, 1 equiv.) was dissolved in DMSO (4 mL, 56.3 mmol, 17.6 equiv). Then $BF_3 \cdot Et_2O$ (0.012 mL, 0.1 mmol, 0.03 equiv) was added. The mixture was heated at 80 °C and stirred for 22 h. Water (10 mL) was added and the organic layer was extracted with CH_2Cl_2 (4x10 mL). The organic layers were combined, dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (cyclohexane/EtOAc 98:2 to 80:20) to give the unreacted starting material **2** (0.41 g, 41 %, R_f =0.7 in cyclohexane/EtOAc

90:10) and the title compound **3** (0.45 g, 43 %, R_f =0.4 in cyclohexane/EtOAc 90:10) as a white solid (mp = 36–40 °C). 1H NMR (300 MHz, $CDCl_3$) (1:1 mixture of regioisomers): δ_H = 0.85 (t, 3H, J =6.4), 1.15–1.38 (m, 17H), 1.38–1.70 (m, 6H), 1.70–1.88 (m, 1H), 2.28 (t, 2H, J =7.4), 2.31–2.53 (m, 2H), 3.15–3.40 (m, 1H), 3.64 (s, 3H), 4.09–4.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) (1:1 mixture of regioisomers): δ_C = 14.2 (CH_3), 22.7, 23.6, 23.7, 24.93 and 24.96, 29.0, 29.08 and 29.11, 29.17 and 29.19, 29.32 and 29.34, 29.4, 29.52 and 29.56, 31.89 and 31.93 (11 CH_2), 33.81 and 33.87 (CH_2), 34.11 and 34.14 (CH_2), 37.88 and 37.95 (CH_2), 51.5 (CH_3), 76.45 and 76.52 (CH), 174.33 and 174.38 (C), 212.59 and 212.64 (C). See supporting information for full characterization.

Procedure for the thiazolylidene-catalysed cleavage of α -hydroxyketone (3) under microwave conditions: In a 5-mL microwave tube, α -hydroxyketone **3** (1:1 mixture of regioisomers) (65.7 mg, 0.2 mmol, 1 equiv), 3,4,5-trimethylthiazol-3-ium iodide **4** (10.2 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (5.5 mg, 0.04 mmol, 20 mol%) were added. The tube was flushed with argon and dry CH_3CN (2 mL) was added. The mixture was stirred under microwave irradiation at the desired temperature for a period of time. The mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. The residue was analyzed by GC using hexadecane as internal standard.

Procedure for the thiazolylidene-catalysed cleavage of α -hydroxyketone (3) with recovery of aldehydes by distillation: In a 25-mL bottom flask, under an argon atmosphere, K_2CO_3 (1.09 mmol, 150.6 mg, 9 mol%) was added to thiazolium salt **16** (359.4 mg, 1.21 mmol, 10 mol%) in dry CH_3CN (4 mL). The mixture was magnetically stirred at room temperature for 10 minutes to give a yellow solution. Then, under argon, the resulting solution was collected by a syringe and injected into a distillation flask containing the starting material **3** (4.00 g, 12.18 mmol). The residue was washed with CH_3CN . The solvent used for the generation of the carbene was evaporated first under reduced pressure (4–6 mbar). Then, the mixture was heated at 180°C and stirred for 3 hours. The distillate was collected between 58 °C and 91 °C under 4–6 mbar to give 2.31 g (58 %m yield) of nonanal **5** and methyl 9-oxononanoate **6** as a 66:34 mixture as determined by GC analysis. The residue (1.69 g, 42 %m yield) was recovered as a 76:24 mixture of starting material **3** and acyloin **8** as determined by GC analysis. If required, the aldehydes could be further separated by flash chromatography (cyclohexane/EtOAc 99.8:0.2 to 95:5).

Keywords: α -hydroxyketone • aldehydes • methyl oleate • organocatalysis • retro-benzoin

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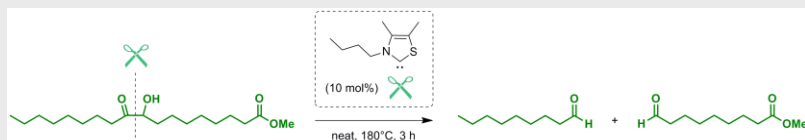
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Title

Layout 2:

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Elsa Deruer, Dr. Nicolas Duguet, Prof.
Marc Lemaire****Page No. – Page No.****Thiazolylidene-Catalysed Cleavage of
Methyl Oleate-Derived α -
Hydroxyketone to the Corresponding
Free Aldehydes**

The α -hydroxyketone derived from methyl oleate was cleaved under non-oxidative conditions to give the corresponding aldehydes. The reaction proceeds through a retro-benzoin process catalyzed by a thiazolylidene species. The aldehydes produced are in equilibrium with their corresponding symmetric acyloins and could be recovered by distillation.