EurJOC
European Journal of Organic Chemistry

Communications
doi.org/10.1002/ejoc.202100053

Chemistry Europe
European Chemical Societies Publishing

Synthesis of Imidazoles from Fatty 1,2-Diketones

Mansouria Bouchakour,[a, b] Mortada Daaou,[b] and Nicolas Duguet*[a]

Unsaturated vegetable oils and their corresponding fatty acid derivatives constitute interesting renewable platforms for the preparation of heterocycles, notably through the formation of oxygenated intermediates. In this work, fatty imidazoles were prepared from the corresponding 1,2-diketones through Debus-Radziszewski reaction. The reaction was optimized under microwave irradiation using a 1,2-diketone derived from methyl oleate and ammonium acetate as a nitrogen source. Using benzaldehyde as a model substrate, the reaction occurs at 180 °C for 5 min and the desired imidazole was formed in 96% GC yield. A range of aldehydes was tested under the optimized conditions and the corresponding imidazoles were obtained in 33–99% isolated yields (20 examples).

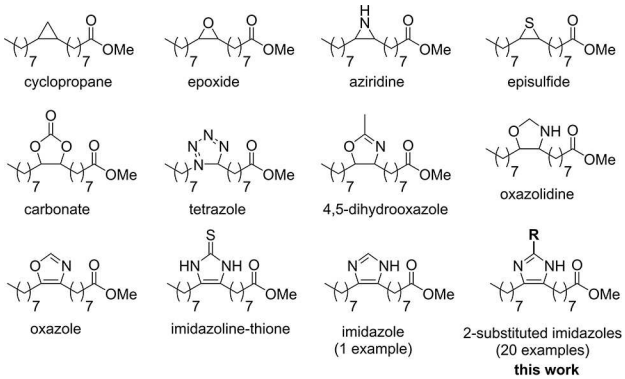
The imidazole core is naturally occurring in some molecules of life such as histidine and histamine and is also present in a wide range of natural products.[1] Moreover, it is encountered in many biologically active molecules exhibiting a wide variety of properties such as anti-inflammatory[2] and inhibition of p38 MAP kinase.[3] Furthermore, some of imidazole-containing molecules have also antiviral,[4] antimicrobial,[5] antifungal[6] and antitumoral[7] activities. In addition to these biologically-relevant properties, imidazoles are also encountered in organic chemistry such as in carbonyldiimidazole (CDI),[8] ionic liquids[9] and *N*-heterercyclic carbenes, that serve both as organocatalysts[10] or ligands[11] for organometallic complexes.

The Debus–Radziszewski reaction allows the straightforward synthesis of imidazoles from 1,2-diketones, aldehydes and a source of ammonia such as ammonium acetate.[12] In this respect, it is a useful multi-component reaction (MCR) that can be used to generate libraries of compounds.[13] A large variety of catalysts have been reported to promote the reaction including organocatalysts,[14] (acidic) ionic liquids,[15] Brönsted acids,[16] Lewis acids[17] and their supported versions,[18] and metal oxides.[19] In this vast field, recent advances concern the use magnetically recoverable catalytic systems.[20] Alternatively, catalyst-free conditions,[21] notably using microwave irradiation,[22] are particularly interesting considering that imidazoles are biologically-relevant targets that should be exempt of any traces of metals.

Most of reported methods are only focussing on the preparation of imidazoles from aromatic substrates such as benzil or benzoin derivatives. In sharp contrast, the use of aliphatic α-hydroxyketones or 1,2-diketones has been by far less studied and it usually only concerns butanedione or acetoin.

Vegetable oils are interesting renewable resources for the chemical industry. For example, they can be transformed to biodiesel,[23] fine chemicals[24] and polymers.[25] Considering their low environmental impact, they have already found numerous applications in paints, packaging materials, lubricants, surfactants, cosmetics and pharmaceuticals. Unsaturated fatty derivatives are particularly interesting as they can be functionalized to give a wide range of reactive groups such as aldehydes, ketones, 1,2-diols, α-hydroxyketones and diketones.[24] Moreover, the double bond is an excellent site for the construction of carbocycles such as cyclopropanes[26] and heterocycles such as epoxides,[27] aziridines,[28] episulfides[29] and carbonates (Scheme 1).[30] In particular, Fürmeier and Metzger have shown that nitrogenated heterocycles can be produced from unsaturated fatty acids such as tetrazoles, 4,5-dihydrooxazoles, oxazolidines, oxazoles and imidazoline-thione.[31] To the best of our knowledge, only one example of a fatty imidazole was reported by the authors,[31] obtained by reacting a fatty α-hydroxyketone with formamide through a Bredereck reaction.[32]

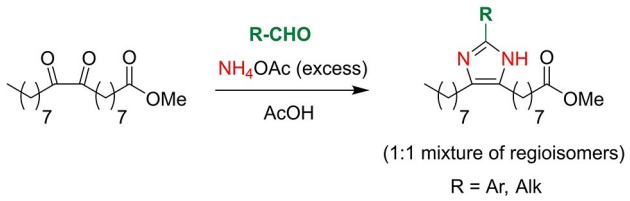
Within the frame of a research programme aiming at the valorization of vegetable oil derivatives,[33] we have recently reported a clean access to fatty α-hydroxyketones from the corresponding 1,2-diols by either palladium-catalyzed selective oxidation using oxygen as a clean oxidant or by ruthenium-



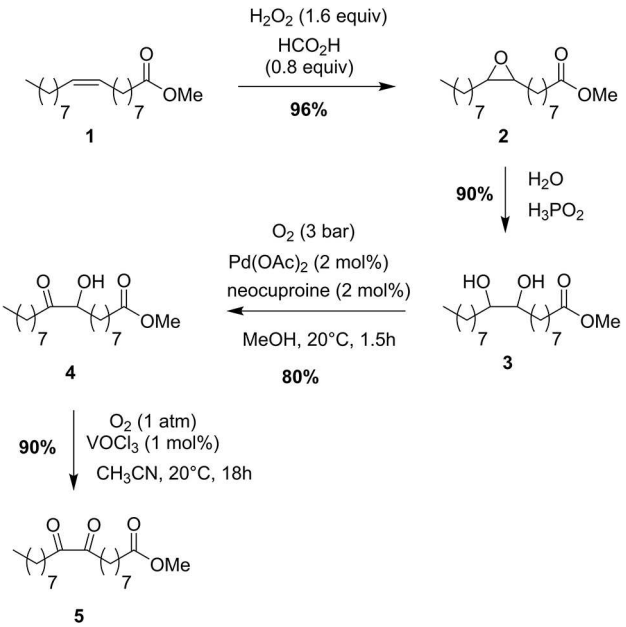
Scheme 1. Selected heterocycles from unsaturated fatty acids (represented for methyl oleate, some are mixture of regioisomers).

[a] *M. Bouchakour, Dr. N. Duguet*
Univ Lyon, CNRS, INSA-Lyon, CPE-Lyon, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires,
ICBMS, UMR 5246, Equipe CAtalyse, SYnthèse et ENvironnement (CASYEN), Université Claude Bernard Lyon 1
Bâtiment Lederer, 1 rue Victor Grignard, 69100 Villeurbanne, France
E-mail: nicolas.duguet@univ-lyon1.fr
[b] *M. Bouchakour, Prof. M. Daaou*
Faculté de Chimie, Département de Chimie Organique Industrielle
Laboratoire de Synthèse organique, Physico-chimie, Biomolécules et Environnement (LSPBE)
Université des Sciences et de la Technologie d'Oran (USTO) Mohamed Boudiaf
BP 1505, El'Mnaouer, Oran, 31000, Algeria

catalyzed dehydrogenation.[33b] Moreover, the corresponding fatty 1,2-diketones were also prepared by oxidation of α-hydroxyketones, using oxygen.[33f] With a clean access to fatty 1,2-diketones in hands, we now report the synthesis of imidazoles from these starting materials through Debus–Radziszewski reaction (Scheme 2).



Scheme 2. Imidazoles from fatty 1,2-diketones through Debus-Radziszewski reaction.



Scheme 3. Preparation of fatty 1,2-diketone from methyl oleate.

Table 1. Optimization of reaction conditions.[a]

Entry	NH_4OAc (equiv)	T [°C]	Conv.[b] **5** [%]	GC Yield[b] **6** [%]
1	2	180	77	70
2	2.5	180	93	83
3	3	180	99	91
4	5	180	>99	98
5	10	180	>99	95
6	5	120	85	75
7	5	140	96	91
8	5	160	>99	99

[a] Reaction conditions: 10-mL microwave tube, diketone **5** (65 mg, 0.2 mmol), benzaldehyde (0.2 mmol, 1 equiv), NH_4OAc (2-10 equiv), AcOH (2 mL), 120–180 °C, 5 min. [b] Conversion and yields were determined by gas chromatography using hexadecane as an internal standard.

The 1,2-diketone derived from methyl oleate was selected a model substrate for the optimization of the reaction parameters considering that methyl oleate is by far the most available fatty acid methyl esters. It was prepared through a four-step sequence from commercially available methyl oleate (96% purity) (Scheme 3). First, methyl oleate **1** was epoxidized using H_2O_2 in the presence of formic acid to give epoxide **2** in 96% yield. Next, hydrolysis of the epoxide gave the corresponding 1,2-diol **3** in 90% yield. Then, fatty α-hydroxyketone **4** was prepared by selective oxidation using oxygen (3 bar) in the presence of $Pd(OAc)_2$ and neocuproine and was isolated in 80%. Finally, oxidation of the α-hydroxyketone under oxygen (1 atm) in the presence of $VOCl_3$ gave the desired 1,2-diketone **5** in 90% yield (62% overall yield over 4 steps).

First, the reaction was carried out using benzaldehyde (1 equiv) and 2 equivalents of ammonium acetate in acetic acid (Table 1). After only 5 min at 180 °C under microwave irradiation,[22] the conversion of **5** reached 77% and the desired imidazole **6** was obtained in 70% GC yield (Table 1, entry 1). Progressively increasing the amount of NH_4OAc from 2 to 5 equivalents led to an increase in both conversion and yield (Table 1, entries 2–4). Satisfyingly, with 5 equivalents, the conversion was complete and the yield of imidazole **6** reached 98% (Table 1, entry 4). Further increasing the amount to 10 equivalents led to a slight decrease of yield to 95%, probably due to the formation of side-products (Table 1, entry 5). The effect of the temperature was also studied using 5 equivalents of NH_4OAc. From 120 to 160 °C, the conversion increased from 85 to >99% and the yield of **6** from 75 to 99% (Table 1, entries 6–8). This indicates that the reaction was also very efficient at 160 °C, however, we preferred to select a temperature of 180 °C for further studies, notably for the conversion of less reactive aldehydes.

The scope was first investigated under the optimized conditions using aromatic aldehydes [aldehyde (1 equiv), NH_4OAc (5 equiv), 180 °C, 5 min)] (Figure 1). With benzaldehyde, fatty imidazole **6** was obtained in 60% isolated yield, after purification by column chromatography. The moderate yield obtained is explained by the fact that the purification of such species proved to be laborious, probably due to their amphiphilic nature. Starting from 4-phenylbenzaldehyde and 4-anisaldehyde, imidazoles **7** and **8** were obtained in 51 and 33% yield. The influence of the substitution pattern of the aromatic aldehydes was studied using *ortho*-, *meta*- and *para*-tolualdehyde. Expectedly, the yield of fatty imidazole **9** (with para-tolualdehyde) was found to be superior to those of imidazoles **10** and **11** bearing *meta*- and *ortho*-methyl substituent, probably for steric reasons.

Para-halogenated benzaldehydes were also considered. With a bromine, chlorine and flurorine, the corresponding imidazoles **12**–**14** were isolated in 50, 43 and 45% yield, respectively. 1- and 2-naphthaldehyde gave imidazoles **15** and **16** in 45 and 47% yields, respectively. More challenging

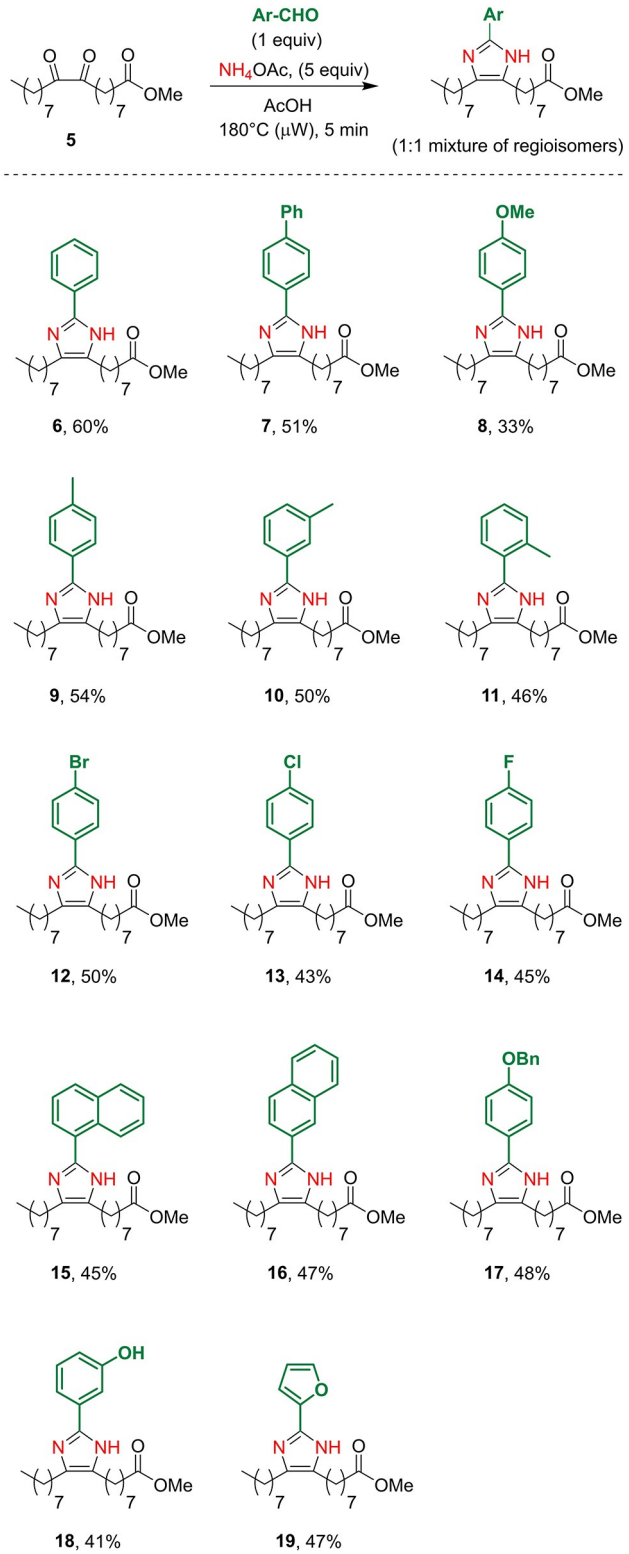


Figure 1. Scope of aromatic aldehydes for the synthesis of fatty imidazoles.

aldehydes, such as 4-(benzyloxy)benzaldehyde, 3-hydroxybenzaldehyde and furfural were considered. Imidazole **17** was only formed in 48% yield due to the difficulty to fully convert the aldehyde. Imidazole **18** was also obtained in only 41% yield, indicating that the free hydroxyl group has a negative impact on the reaction outcome. Finally, fatty imidazole **19**, incorporating a furfural moiety, was isolated in 47% yield.

The scope of the reaction was also investigated with diketone **5** using a range of aliphatic aldehydes (Figure 2). Paraformaldehyde was used as a source of formaldehyde and the desired imidazole **20** was obtained in an excellent 98% yield. Linear aliphatic aldehydes were also considered such as butanal, nonanal and dodecanal. Satisfyingly, the corresponding products **21**–**23** were isolated in 77–99% yield. Using branched aldehydes such as isobutyraldehyde and pivalaldehyde gave fatty imidazoles **24** and **25** in 98 and 80% yield, respectively. Overall, aliphatic aldehydes are giving better results than aromatic aldehydes, due to the fact that they are more reactive. Consequently, almost no by-product was formed when using aliphatic aldehydes. In most cases, the crude product did not require further purification by column chromatography after the work-up of the reaction, so the desired fatty imidazoles were isolated with high yields.

Considering that fatty diketone **5** was prepared from the corresponding α-hydroxyketone **4**, we envisioned that the Debus–Radziszewski reaction could also be carried out from this substrate (Table 2). The reaction was first performed under an argon atmosphere, however, the desired product **6** was obtained with only 17% GC ratio under these conditions (Table 2, entry 1). Interestingly, fatty imidazole **26**, bearing a *N*-benzyl group, was formed in 78% GC ratio under these conditions. Consequently, the reaction was repeated under oxygen atmosphere, either to promote the initial oxidation of **4** to diketone **5** or to facilitate the final oxidation of an imidazoline to the imidazole core (Table 2, entry 2). However, the GC ratio of imidazole **6** dropped to 6% under these conditions. Nevertheless, *N*-benzylated imidazole **26** was still obtained as the major product (80% GC ratio), along with an unidentified

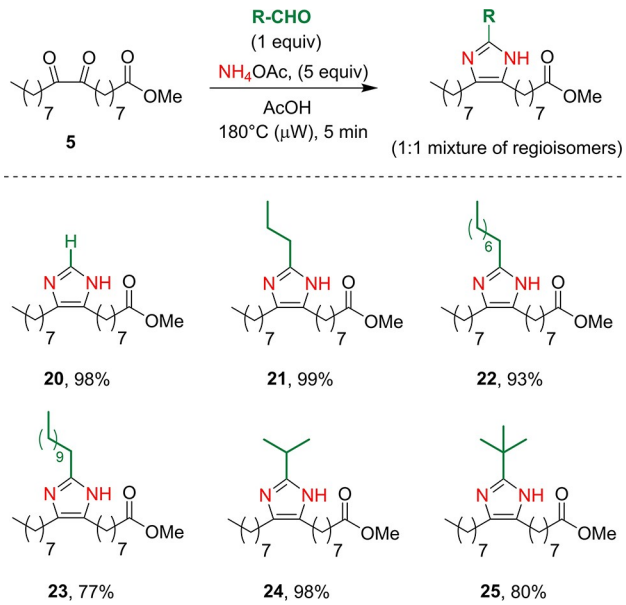
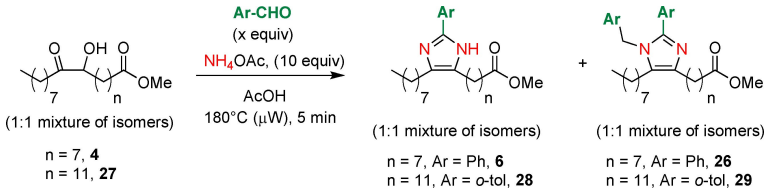


Figure 2. Scope of aliphatic aldehydes for the synthesis of fatty imidazoles.

Table 2. Debus–Radziszewski reaction from fatty α-hydroxyketones.[a]



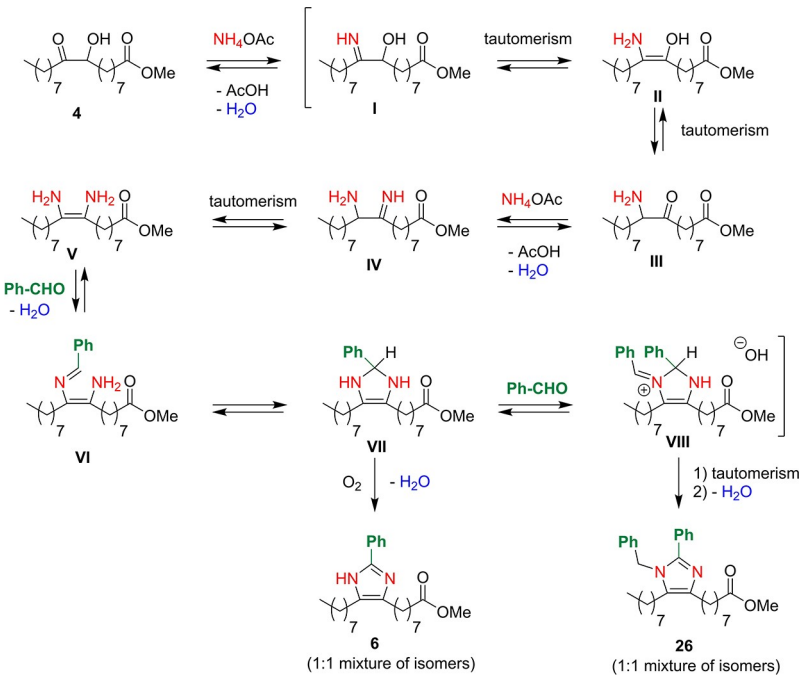
Entry	Atmosphere	ArCHO (equiv)	Conv.[b] **4** (or **27**) [%]	GC ratio[b] **X:6(28):26(29)** [%]
1[c]	Ar	Ph (1)	>99	5:17: 78
2[c]	O_2	Ph (1)	>99	14:6:80
3[c]	Ar	Ph (2)	>99	0:4:96 (59%)[e]
4[d]	Ar	*o*-tol (2)	>99	0:4:96

[a] Reaction conditions: 10-mL microwave tube, α-hydroxyketone **4** or **27** (0.4 mmol), benzaldehyde or *ortho*-tolualdehyde (1 or 2 equiv), NH_4OAc (308 mg, 4 mmol, 10 equiv), AcOH (2 mL), 180 °C, 5 min. [b] Conversion and GC ratio were determined by gas chromatography. **X** represents an unidentified byproduct. [c] Using α-hydroxyketone **4**. [d] Using α-hydroxyketone **27**. [e] Isolated yield in brakets.

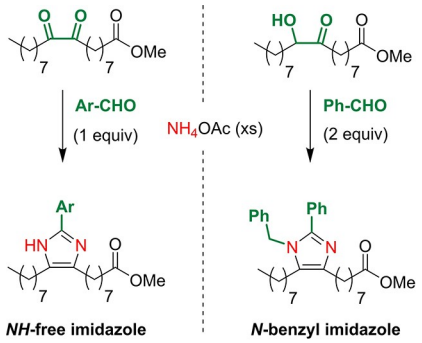
by-product. Considering that **26** is a compound of interest, the reaction was repeated using 2 equivalents of benzaldehyde under argon atmosphere (Table 2, entry 3). Under these conditions, the product was obtained in 96% GC ratio and was isolated in 59% after purification by column chromatography. Finally, the reaction was also performed using α-hydroxyketone **27**, derived from methyl erucate, and *ortho*-tolualdehyde as a bulkier aldehyde (Table 2, entry 4). Satisfyingly, the desired imidazole **29** was also obtained with 96% GC ratio. This result shows that the use of a more sterically demanding aldehyde does not affect the ratio between *NH*-free and *N*-benzyl derivatives.

The formation of **26** from α-hydroxyketone **4** would involve a condensation with a first equivalent of ammonia to form an imine **I** that tautomerizes to **II**, then to an α-aminoketone **III** (Scheme 4).

A second condensation with ammonia would give imine **IV** that tautomerizes to diamine **V**. This diamine would form an imine **VI** in the presence of benzaldehyde, followed by ring closure to give a fatty imidazoline **VII**. Oxidation of intermediate **VII** gives imidazole **6**. Alternatively, imidazoline **VII** could react with a second equivalent of benzaldehyde to form iminium **VIII**, that tautomerizes to give *N*-benzylated imidazole **26** upon dehydration. This final tautomerization is driven by the aromatisation of the imidazoline to the imidazole. An alternative mechanism is also possible, in which benzaldehyde first reacts with ammonium acetate to give benzylamine, that adds onto either **4** or intermediate **III** to give the desired imidazole



Scheme 4. Mechanism proposal for the formation of *N*-benzylated fatty imidazole **26** using two equivalents of aldehydes under argon atmosphere.



Scheme 5. Complementarity between Debus-Radziszewski reactions using fatty diketone or α-hydroxyketone.

26, after addition of a second equivalent of benzaldehyde and subsequent aromatisation. This would be similar to the reported four-component reactions using benzaldehyde and benzylamine to produce tetra-substituted imidazoles from α-hydroxyketones.[15c,34] This alternative mechanism would require the presence of oxygen or air for the final oxidation step. However, it cannot be fully ruled out that the presence of adventitious oxygen is involved.

Overall, Debus–Radziszewski reactions on either α-hydroxyketone or diketone are complementary considering that they are giving the *N*-benzylated or the *NH*-free imidazole, respectively (Scheme 5).

To conclude, we have reported here the preparation of fatty imidazoles from a 1,2-diketone derived from methyl oleate through a Debus–Radziszewski reaction. The reaction was optimized under microwave irradiation using a stoichiometric amount of aldehyde and an excess of ammonium acetate in acetic acid. A range of aromatic and aliphatic aldehydes were tested and the corresponding fatty imidazoles were obtained in 33–99 % isolated yields (20 examples). Interestingly, the reaction affords the *N*-benzylated imidazole when starting from the corresponding α-hydroxyketone using 2 equivalents of benzaldehyde.

Acknowledgements

The authors thank the "Université des Sciences et de la Technologie d'Oran (USTO) Mohamed Boudiaf" (Algeria) for a preliminary grant for M.B. The Algerian "Ministry of Higher Education and Scientific Research" is also acknowledged for further financial support to M.B. within the frame of the "Programme National Exceptionnel" (PNE, 2019–2020). "La Direction Générale de la Recherche Scientifique et du Développement Technologique (DGRSDT)" is also thanked for financial support. T. De Dios Miguel (team CASYEN, ICBMS) is acknowledged for sharing some fatty diketone.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Aldehydes · Debus-Radziszewski reaction · 1,2-Diketones · Fatty acids · Imidazoles

[1] a) Z. Jin, *Nat. Prod. Rep.* **2009**, *26*, 382–445; b) Z. Jin, *Nat. Prod. Rep.* **2006**, *23*, 464–496; c) Z. Jin, *Nat. Prod. Rep.* **2005**, *22*, 196–229; d) D. J. Newman, G. M. Cragg, K. M. Snader, *J. Nat. Prod.* **2003**, *66*, 1022–1037.
[2] J. G. Lombardino, E. H. Wiseman, *J. Med. Chem.* **1974**, *17*, 1182–1188.
[3] J. A. Murry, *Curr. Opin. Drug Discovery Dev.* **2003**, 6, 945.
[4] D. Sharma, B. Narasimhan, P. Kumar, V. Judge, R. Narang, E. De Clercq, J. Balzarini, *Eur. J. Med. Chem.* **2009**, 44, 2347–2353.
[5] M. Antolini, A. Bozzoli, C. Ghiron, G. Kennedy, T. Rossi, A. Ursini, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1023–1028.
[6] J. Heers, L. J. J. Backx, J. H. Mostmans, J. Van Cutsem, *J. Med. Chem.* **1979**, *22*, 1003–1005.
[7] L. Wang, K. W. Woods, Q. Li, K. J. Barr, R. W. McCroskey, S. M. Hannick, L. Gherke, R. B. Credo, Y.-H. Hui, K. Marsh, R. Warner, J. Y. Lee, N. Zielinski-Mozng, D. Frost, S. H. Rosenberg, H. L. Sham, *J. Med. Chem.* **2002**, *45*, 1697–1711.
[8] A. Armstrong, *e-EROS Encycl. Reagents Org. Synth.* **2007**, 1–8.
[9] D. Zheng, L. Dong, W. Huang, X. Wu, N. Nie, *Renewable Sustainable Energy Rev.* **2014**, *37*, 47–68.
[10] a) X. Bugaut, F. Glorius, *Chem. Soc. Rev.* **2012**, *41*, 3511–3522; b) C. D. Campbell, K. B. Ling, A. D. Smith, in *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis* (Ed. C. S. J. Cazin), Springer, Netherlands, **2011**, pp. 263–297; c) P.-C. Chiang, J. W. Bode, in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools* (Ed. S. Díez-González), Royal Society of Chemistry, Cambridge, **2010**, pp. 339–445; d) E. M. Phillips, A. Chan, K. A. Scheidt, *Aldrichimica Acta* **2009**, *42*, 55–66; e) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606–5655; f) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000; *Angew. Chem.* **2007**, *119*, 3046–3058.
[11] a) S. P. Nolan, *N*-Heterocyclic Carbenes in Synthesis, Wiley-VCH, **2006**; b) G. Fortman, S. P. Nolan, *Chem. Soc. Rev.* **2011**, *40*, 5151–5169.
[12] a) H. Debus, *Justus Liebigs Ann. Chem.* **1858**, *107*, 199–208; b) Br. Radziewski, *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 2706–2708.
[13] a) E. Ruijter, R. Scheffelaar, R. V. A. Orru, *Angew. Chem. Int. Ed.* **2011**, *50*, 6234–6246; *Angew. Chem.* **2011**, *123*, 6358–6371; b) A. Dömling, W. Wang, K. Wang, *Chem. Rev.* **2012**, *112*, 3083–3135; c) B. H. Rotstein, S. Zaretsky, V. Rai, A. K. Yudin, *Chem. Rev.* **2014**, *114*, 8323–8359.
[14] a) S. Narayana Murthy, B. Madhav, Y. V. D. Nageswar, *Tetrahedron Lett.* **2010**, *51*, 5252–5257; b) S. Samai, G. Chandra Nandi, P. Singh, M. S. Singh, *Tetrahedron* **2009**, *65*, 10155–10161; c) N. V. Shitole, K. F. Shelke, S. S. Sonar, S. A. Sadaphal, B. B. Shingate, M. S. Shingare, *Bull. Korean Chem. Soc.* **2009**, *30*, 1963–1966.
[15] a) S. A. Siddiqui, U. C. Narkhede, S. S. Palimkar, T. Daniel, R. J. Lahoti, K. V. Srinivasan, *Tetrahedron*, **2005**, *61*, 3539–3546; b) D. Fang, J. Yang, C. Jiao, *Catal. Sci. Technol.* **2011**, *1*, 243–245; c) B. Maleki, G. E. Kahoo, R. Tayebee, *Org. Prep. Proced. Int.* **2015**, *47*, 461–472; d) W. A. A. Arafa, *RSC Adv.* **2018**, *8*, 16392–16399.
[16] a) N. D. Kokare, J. N. Sangshetti, D. B. Shinde, *Synthesis* **2007**, 2829–2834; b) N. Chouha, T. Boumoud, I. Tebabel, B. Boumoud, A. Debache, *Der Pharma Chemica*, **2016**, *8*, 202–206; c) K. D. Dhawale, N. M. Thorat, L. R. Patil, *Asian J. Chem.* **2017**, *29*, 1709–1712.
[17] a) S. D. Sharma, P. Hazarika, D. Konwar, *Tetrahedron Lett.* **2008**, *49*, 2216–2220; b) M. V. Marques, M. M. Ruthner, L. A. M. Fontoura, D. Russowsky, *J. Braz. Chem. Soc.* **2012**, *23*, 171–179; c) R. Wang, C. Liu, G. Luo, *Green Chem. Lett. Rev.* **2010**, *3*, 101–104; d) S. Agarwal, M. Kidwai, R. Poddar, M. Nath, *ChemistrySelect* **2017**, *2*, 10360–10364.
[18] a) J. Safari, S. D. Khalili, S. H. Banitaba, *Synth. Commun.* **2011**, *41*, 2359–2373; b) Á. Magyar, Z. Hell, *Synlett* **2019**, *30*, 89–93.
[19] a) N. Thimmarajuab, S. Z. M. Shamshuddin, *RSC Adv.* **2016**, *6*, 60231–60243; b) K. Bahrami, M. M. Khodaei, A. Nejati, *Monatsh. Chem.* **2011**, *142*, 159–162.
[20] a) M. Nejatianfar, B. Akhlaghinia, R. Jahanshahi, *Appl. Organomet. Chem.* **2018**, *32*, e4095; b) H. Singh, J. K. Rajput, *Appl. Organomet. Chem.* **2018**, *32*, e3989; c) L. Z. Fekri, M. Nikpassand, S. Shariati, B. Aghazadeh, R. Zarkeshvari, N. N. pour, *J. Organomet. Chem.* **2018**, *871*, 60–73; d) Z.

Zarnegar, J. Safari, *New J. Chem.* **2014**, *38*, 4555–4565; e) M. Kalhor, Z. Zarnegar, *RSC Adv.* **2019**, *9*, 19333–19346; f) J. Safari, Z. Zarnegar, *Ultrason. Sonochem.* **2013**, *20*, 740–746.
[21] a) M. Wang, J. Gao, Z. Song, *Prep. Biochem. Biotechnol.* **2010**, *40*, 347–353; b) K. Pradhan, B. K. Tiwary, M. Hossain, R. Chakraborty, A. K. Nanda, *RSC Adv.* **2016**, *6*, 10743–10749; c) L. Kong, X. Lv, Q. Lin, X. Liu, Y. Zhou, Y. Jia, *Org. Process Res. Dev.* **2010**, *14*, 902–904.
[22] a) J. F. Zhou, G. X. Gong, H. Q. Zhu, F. X. Zhu, *Chin. Chem. Lett.* **2009**, *20*, 1198–1200; b) E. Chauveau, C. Marestin, F. Schiets, R. Mercier, *Green Chem.* **2010**, *12*, 1018–1022; c) S. E. Wolkenberg, D. D. Wisnoski, W. H. Leister, Y. Wang, Z. Zhao, C. W. Lindsley, *Org. Lett.* **2004**, *6*, 1453–1456; d) J.-F. Zhou, Y.-Z. Song, Y.-L. Yang, Y.-L. Zhu, S.-J. Tu, *Synth. Commun.* **2005**, *35*, 1369–1373; e) J.-F. Zhou, G.-X. Gong, X.-J. Sun, Y.-L. Zhu, *Synth. Commun.* **2010**, *40*, 1134–1141.
[23] a) F. Ma, M. A. Hanna, *Bioresour. Technol.* **1999**, *70*, 1–15; b) A. Srivastava, R. Prasad, *Renewable Sustainable Energy Rev.* **2000**, *4*, 111–13; c) A. Demirbas, *Appl. Energy* **2011**, *88*, 17–28.
[24] a) U. Biermann, W. Friedt, S. Lang, W. Lìhs, G. Machmìller, J. O. Metzger, M. Rìsch gen. Klaas, H. J. Schfer, M. P. Schneider, *Angew. Chem. Int. Ed.* **2000**, *39*, 2206–2224; ; *Angew. Chem.* **2000**, *112*, 2292–2310; ; b) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer, *Angew. Chem. Int. Ed.* **2011**, *50*, 3854–3871; *Angew. Chem.* **2011**, *123*, 3938–3956; c) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1788–1802; d) Y. Xia, R. C. Larock, *Green Chem.* **2010**, *12*, 1893–1909; e) J. M. Fraile, J. I. García, C. I. Herrerías, E. Pires, *Synthesis*, **2017**, *49*, 1444–1460.
[25] a) Y. Xia, R. C. Larock, *Green Chem.* **2010**, *12*, 1893–1909; b) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1788–1802.
[26] a) M. S. F. Lie Ken Jie, W. L. K. Lam, *J. Chem. Soc. Chem. Commun.* **1987**, *19*, 1460–1461; b) M.-L. Kwan, A. Mirjafari, J. R. McCabe, R. A. O'Brien, D. F. Essi IV, L. Baum, K. N. West, J. H. Davis Jr., *Tetrahedron Lett.* **2013**, *54*, 12–14; c) J. W. Palko, P. H. Buist, J. M. Manthorpe, *Tetrahedron: Asymmetry* **2013**, *24*, 165–168.
[27] a) Y. Wei, G. Li, Q. Lv, C. Cheng, H. Guo, *Ind. Eng. Chem. Res.* **2018**, *57*, 16284–16294; b) A. Campanella, C. Fontanini, M. A. Baltanas, *Chem. Eng. J.* **2008**, *144*, 466–475; c) Z. S. Petrovic, A. Zlatanić, C. C. Lava, S. Sinadinović-Fišer, *Eur. J. Lipid Sci. Technol.* **2002**, *104*, 293–299; d) M. Guidotti, R. Psaro, N. Ravasio, M. Sgobba, E. Gianotti, S. Grinberg, *Catal. Lett.* **2008**, *122*, 53–56.
[28] a) S. Fürmeier, J. O. Metzger, *Eur. J. Org. Chem.* **2003**, 649–659; b) M. S. F. Lie Ken Jie, M. S. K. Syed-Rahmatullah, *J. Am. Oil Chem. Soc.* **1992**, *69*, 359–362.
[29] M. S. F. Lie Ken Jie, Y. F. Zheng, *Chem. Phys. Lipids* **1988**, *49*, 167–178.
[30] a) J. Laganke, L. Greiner, W. Leitner, Walter, *Green Chem.*, **2013**, *15*, 1173–1182; b) N. Tenhumberg, H. Büttner, B. Schaffner, D. Kruse, M. Blumenstein, T. Werner, *Green Chem.*, **2016**, *18*, 3775–3788; c) H. Büttner, C. Grimmer, J. Steinbauer, T. Werner, *ACS Sustainable Chem. Eng.*, **2016**, *4*, 4805–4814; d) L. Peña Carrodeguas, A. Cristofol, J. M. Fraile, J. A. Mayoral, V. Dorado, C. I. Herrerias, A. W. Kleij, *Green Chem.*, **2017**, *19*, 3535–3541; e) L. Longwitz, J. Steinbauer, A. Spannenberg, T. Werner, *ACS Catal.*, **2018**, *8*, 665–672; f) F. Chen, Q.-C. Zhang, D. Wei, Q. Bu, B. Dai, N. Liu, *J. Org. Chem.* **2019**, *84*, 11407–11416; g) W. Natongchai, S. Pornpraprom, V. D'Elia, *Asian J. Org. Chem.* **2020**, *9*, 801–810; h) A. Akhdar, K. Onida, N. D. Vu, K. Grollier, S. Norsic, C. Boisson, F. D'Agosto, N. Duguet, *Adv. Sustainable Syst.* **2020**, DOI: 10.1002/adsu.202000218.
[31] S. Fürmeier, J. O. Metzger, *Eur. J. Org. Chem.* **2003**, 885–893.
[32] H. Bredereck, G. Theilig, *Chem. Ber.* **1953**, *86*, 88–96.
[33] a) E. Deruer, N. Duguet, M. Lemaire, *ChemSusChem* **2015**, *8*, 2481–2486; b) N. D. Vu, B. Guicheret, N. Duguet, E. Metay, M. Lemaire, *Green Chem.* **2017**, *19*, 3390–3399; c) N. D. Vu, S. Bah, E. Deruer, N. Duguet, M. Lemaire, *Chem. Eur. J.* **2018**, *24*, 8141–8150; d) B. Guicheret, Y. Bertholo, P. Blach, Y. Raoul, E. Metay, M. Lemaire, *ChemSusChem* **2018**, *11*, 3431–3437; e) A. Charvieux, N. D. Vu, N. Duguet, M. Lemaire, *Eur. J. Org. Chem.* **2019**, 1251–1256; f) N. D. Vu, R. Chavallard, T. De Dios Miguel, N. Duguet, M. Lemaire, *ACS Sustainable Chem. Eng.* **2019**, *7*, 13865–13872; g) B. Guicheret, E. Da Silva, R. Philippe, A. Favre-Reguillon, L. Vanoye, P. Blach, Y. Raoul, C. De Bellefon, E. Metay, M. Lemaire, *ACS Sustainable Chem. Eng.* **2020**, *8*, 13167–13175; h) T. De Dios Miguel, N. D. Vu, M. Lemaire, N. Duguet, *ChemSusChem* **2021**, *14*, 379–386.
[34] a) L. Nagarapu, S. Apuri, S. Kantevari, *J. Mol. Catal. A* **2007**, *266*, 104–108; b) A. Mohammadi, H. Keshvari, R. Sandaroos, B. Maleki, H. Rouhi, H. Moradi, Z. Sepehr, S. Damavandi, *Applied Catal. A: Gen.* **2012**, *429–430*, 73–78; c) B. Maleki, H. Eshghi, A. Khojastehnezhad, R. Tayebee, S. S. Ashrafi, G. E. Kahooa, F. Moeinpour, *RSC Adv.* **2015**, *5*, 64850–64857.

Manuscript received: January 18, 2021
Revised manuscript received: February 24, 2021
Accepted manuscript online: March 1, 2021