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Adding value to terpenoids: from pseudoionone to 1-methyl-1,3-cyclohexadiene

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Alkenes and conjugated dienes play an important role in organic synthesis and polymer chemistry. Being essentially fossil-based materials, there is a strong interest in developing alternative ways to obtain such compounds from renewable resources. In this study, we report the synthesis of 1-methyl-1,3-cyclohexadiene, a cyclic conjugated diene that is rarely reported in the literature and not widely available commercially. This compound is synthesized from pseudoionone using ruthenium-catalysed ring closing olefin metathesis transformation. Mesityl oxide, a known chemical with wide applications, is concomitantly obtained.

Green foundation

1. Advancing the field of Green Chemistry: the synthesis from a biosourced reagent of a rare and fossil-sourced conjugated diene is reported. Regardless of the scale-up, this is yet another example of how biomass can be inspiring and used to replace fossil-based compounds.
2. Green Chemistry achievement: we use a catalytic transformation to obtain the desired product under mild conditions of temperature (70 °C) with yields up to 63%. This synthesis is greener than those previously reported utilising fossil resources and hazardous and/or toxic reagents, with the generation of harmful wastes.
3. This work would benefit from efficient distillation separation (chemical engineering) that would enable the use of greener solvents such as dimethylcarbonate (DMC). A catalyst that would be selective for the transformation of only one stereoisomer from the feed would greatly facilitate the separation of the product of interest. If the product of interest is to be synthesised from an appropriate stereoisomer, its synthesis will need to be improved in terms of green chemistry.

A. Introduction

The utilisation of biomass and biosourced compounds as surrogates for fossil-based fuels and chemicals[1–3] has gained tremendous interest and has been considered a dream turned into reality in the last three decades. Besides food and feed, biomass is increasingly used in a number of areas, such as raw materials in the chemical industry and energy production.[4,5] If biomass can generate high volumes of raw materials of industrial interest, it can also be the source of high-value-added niche compounds obtained in much lower volumes. Terpenes and their derivatives are one of the high-value-added classes of compounds obtained from a variety of plants and trees and are used in the domains of flavours and fragrances (FnFs).[6,7] They are also the source of new synthetic products, provided efficient and selective transformations can be used for the transformation of these sometimes multi-functional compounds. Owing to the isoprene-based structure of terpenes, olefin metathesis[8,9] has been shown to be an efficient and selective catalytic tool for their valorisation,[10–14] including those sterically hindered, for which high reactivity was difficult to predict. Recently, inspired by the work of Robinson,[15] we and other researchers have demonstrated that sterically hindered carbon–carbon double bonds in a variety of cyclic terpenes and terpenoids are, in fact, reactive, provided the productive reaction pathways are triggered by the utilisation of sterically hindered cross-metathesis partners.[16–18] With this in mind, we turned our attention to pseudoionone, a biosourced terpene derivative containing, in principle, poorly reactive carbon–carbon double bonds. Pseudoionone is commonly obtained by the aldol condensation of citral (a mixture of neral and geranial) with acetone under basic conditions (Scheme 1).[19–21]

Only a few examples of ring closing metathesis (RCM) of terpenes have been reported thus far, in particular with linalool, a terpenoid incorporating a terminal carbon–carbon double bond.[13,22,23] The RCM of citronellene, β-myrcene, and β-ocimene, which comprise a terminal carbon–carbon double

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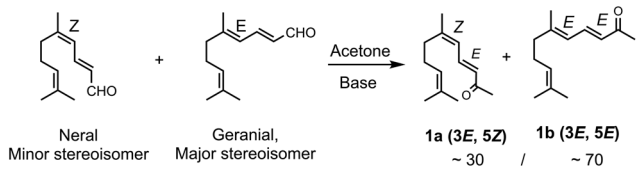
† Equal contributions were made to this work.



Scheme 1 Pseudoionone **1a**/**1b** mixture from citral.

bond, was also reported.[24,25] The transformation of pseudoionone by olefin metathesis has not been reported, and we propose that the RCM of this compound could lead to mesityl oxide **2**,[26,27] a well-known and accessible compound with multiple applications but, more interestingly, could also yield 1-methyl-1,3-cyclohexadiene **3** (Fig. 1).

Indeed, several isomers of methylcyclohexadiene exist, but only few are commercially available at reasonable costs. 1-Methyl-1,3-cyclohexadiene **3** has been used as a reagent in a number of cycloaddition reactions,[28–31] and it could be of interest in polymer synthesis, where polycyclohexadiene has already been investigated.[32–37] To the best of our knowledge, **3** is commercially accessible at a very high cost, and its synthesis requires multiple steps involving toxic and/or hazardous reagents, while being poorly atom economic (Fig. 2).[38–41] Accessing **3** from biomass using a robust and efficient catalytic process would thus be of high interest and we focused our efforts on this objective.

B. Results and discussion

We started our investigations with the metathesis transformation of the commercially available pseudoionone, which consists of a mixture of stereoisomers **1a** and **1b** in a ratio of approximately 29/71, respectively (determined by ^{1}H NMR). Initial attempts were conducted on a 100 mg scale in toluene and the greener dimethylcarbonate,[42,43] the two solvents known to provide similar activities in olefin metathesis,[44,45] using the commercially available 2nd generation Hoveyda pre-catalyst (HII).[46] As depicted in Scheme 2, this transformation proceeded with 90% conversion in DMC (and 88% in toluene), yielding numerous products, most of them being identified using GC/MS (Fig. 3). Notably, the desired product **3** was detected in a substantial amount (38% GC yield), along with **2** (30% GC yield) and other compounds, resulting from cross-metathesis reactions (GC yields determined by calibration with pure **2** and **3** using dodecane as an internal standard). The multiplicity and diversity of the compounds detected is proof that sterically hindered carbon–carbon double bonds, supposedly poorly reactive, are in fact efficiently converted by metathesis. Of note, the identification of **7** resulting from the activation of the precatalyst evidenced the reactivity of the α C=C bond.

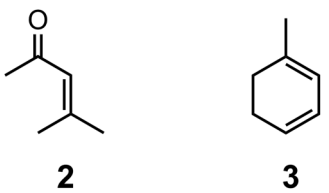


Fig. 1 Mesityl oxide **2** and 1-methyl-1,3-cyclohexadiene **3**.

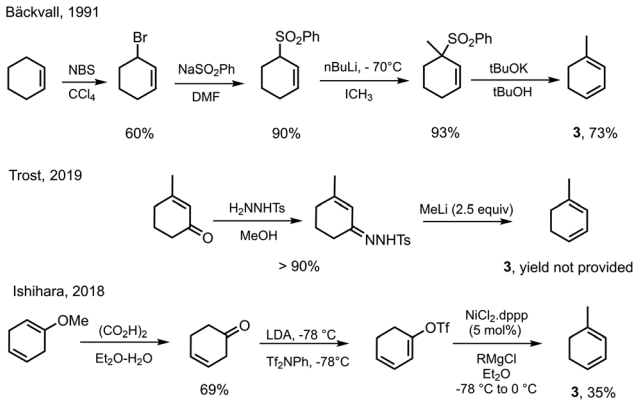
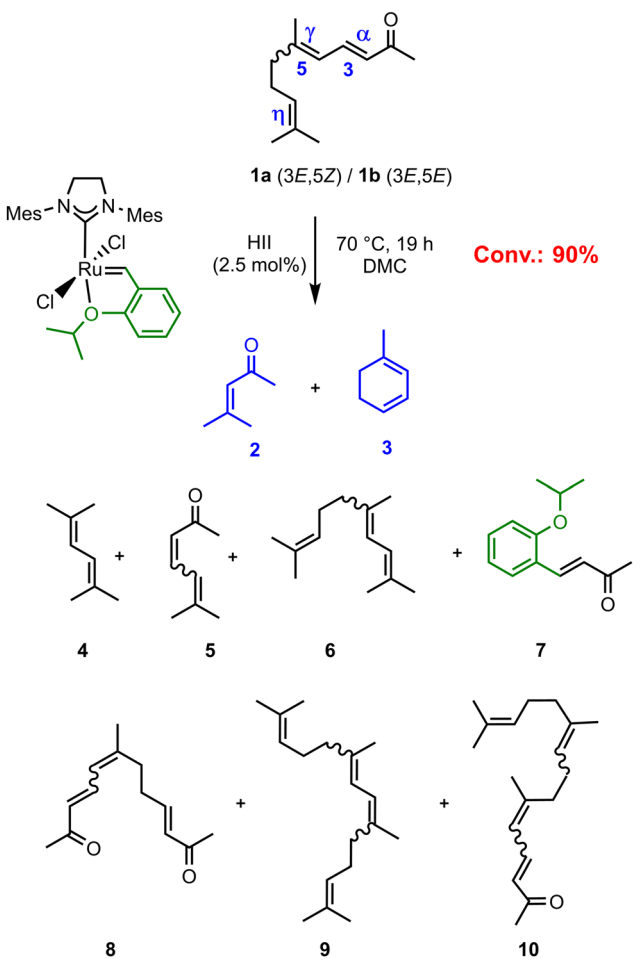


Fig. 2 Reported syntheses of **3**.



Scheme 2 Metathesis transformation of commercial pseudoionone (29% **1a**/71% **1b**; 100 mg; 0.51 mmol).

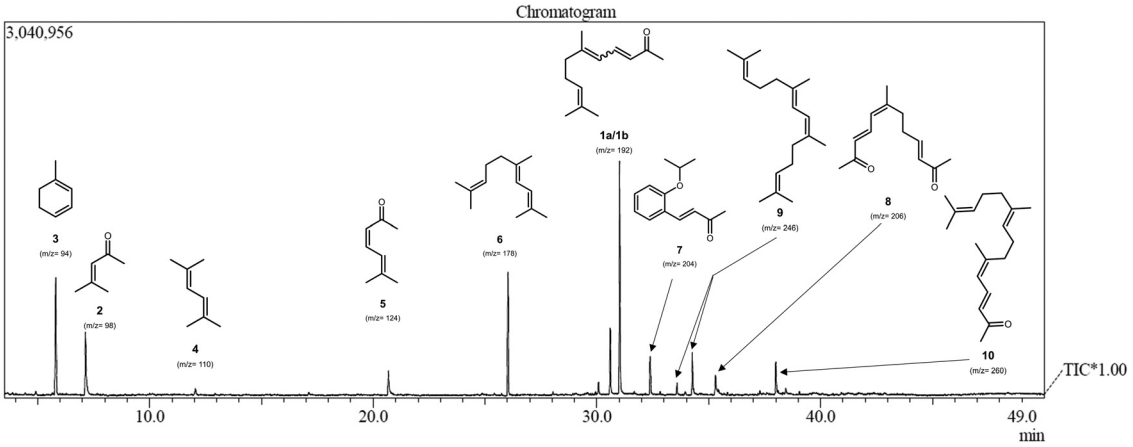
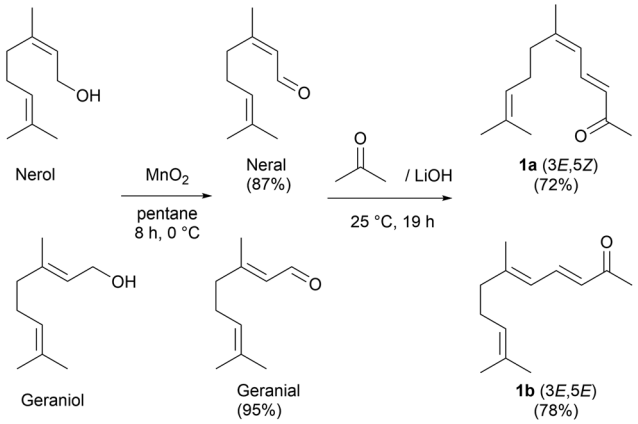


Fig. 3 GC/MS chromatogram of the commercial pseudoionone metathesis reaction.

Following this promising result, we turned our attention to the isolation of **2** and **3**, which proved difficult due to their low and close boiling points of 130 °C (**2**) and 110 °C (**3**) compared to 90 °C for the DMC solvent. To overcome this issue, we moved to high-boiling solvents from which the products of interest could be distilled off. After ruling out diethyl carbonate and xylenes due to their low boiling points (120 °C and approximately 140 °C, respectively), we considered using alkanes. Alkanes are not considered to be the solvents of choice in olefin metathesis due to their poor solvation of organometallic catalysts. As a result, they are rarely used, or even evaluated, in olefin metathesis transformations. Nevertheless, a few reports have shown that high conversions could be obtained in such solvents.[47,48] Interestingly, attempts in decane (b.p. = 172 °C) at 70 °C with 2.5 mol% of HII furnished similarly high conversions (85%) despite the low (visual) solubility of HII in this solvent. However, purification was still not efficient, as some amount of decane was distilled along with compounds **2** and **3**. Hence, we used to paraffin oil as a non-volatile solvent. Here again, the solubility of HII at room temperature was (visually) low, but optimization of reaction temperature and time allowed reaching the highest conversion of 85% at 70 °C. Lowering the catalyst loading to 1 mol% proved detrimental as the conversion dropped to 75%. With both solvents (decane and paraffin oil), the same multiple products were detected by GC, but GC/MS could not be used due to the high boiling point of decane and the non-volatility of paraffin oil. To confirm the reactivity and product distribution in such apolar solvents, the reaction was also performed in cyclohexane, and a GC/MS analysis could be performed, confirming the nature of the products obtained (see SI). Here again, although **2** and **3** are expected to be produced in equimolar amounts, GC yields of 26% and 36% were determined for **2** and **3**, respectively, in paraffin oil, which is similar to the ratio of 30/38 obtained in DMC (*vide supra*). This difference in the ratio of these two compounds will be examined later. As explained earlier, paraffin oil was selected as the solvent to enable the distillation of volatile compounds **2** and **3**. The reaction was thus repeated on a larger scale (1 g) under dynamic vacuum, connecting the reaction vessel (Schlenk tube) to a liquid nitrogen-cooled trap from the onset of the reaction. After 3 h, the fraction collected in the cold trap was analysed by GC/MS and ^{1}H NMR, revealing the presence of **2** and **3** in a 30/70 ratio. Note that this ratio should not be given too much importance, as it depends on the difference in volatility between these two compounds. ^{1}H NMR also evidenced the presence of tetramethylethylene (TME, Scheme 5) in low amounts (<2%, not detected by GC/MS owing to its high volatility and detector cut-off parameter for detector protection). The presence of TME revealed that cross metathesis or ring-closing metathesis between two *gem*-dimethyl-substituted carbon–carbon double bonds occurred during the transformation. The mixture of trapped volatiles was further separated by column chromatography on basic alumina. Here again, the nature and selection of an appropriate solvent for this purification was done according to its ability to separate **2** and **3** and its high boiling point. After several tests, dodecane and dibenzyl ether were found suitable for this separation, although dibenzyl ether decomposed to some extent into toluene and benzaldehyde on alumina (see SI). Thus, following separation on the alumina column, the fractions containing **3** (identified by GC) were collected and submitted to a second distillation under vacuum, which allowed isolating **3** in 31% yield with only 7% of TME.

Clearly, the metathesis process is very complex, and it is difficult to understand and identify the pathways leading to each of the compounds detected. We have therefore continued our studies with the aim of providing answers to the questions raised by these initial results. Hence, we have studied the reactivity of both isomers **1a** and **1b**, prepared individually from nerol and geraniol (Scheme 3).[20] Both products were obtained in acceptable yields subject to rigorous temperature control during the initial oxidation step in order to prevent double-bond isomerisation. **1b** was obtained as a single stereoisomer, while **1a** contained about 2% of **1b**.

The transformation of **1a** was first investigated at 70 °C in paraffin oil using 2.5 mol% HII. This reaction proceeded in



Scheme 3 Synthesis of pure **1a** and **1b**.

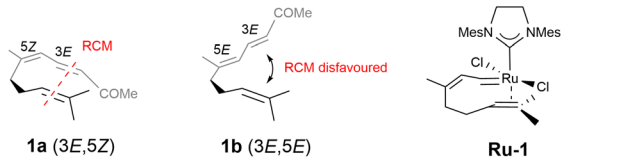


Fig. 4 Conformation of **1a** and **1b** enabling or preventing RCM and **Ru-1** with the prenyl group in the *trans*-position relative to the bulky NHC ligand.

19 h with almost quantitative conversion (98%), yielding **2** and **3** as unique products of the reaction (Scheme 4). Notably, 92% conversion was still obtained when the catalyst loading was lowered to 1 mol%. Purification of compounds **2** and **3** was performed in 3 steps, starting with the trapping of volatiles under vacuum and further separation by column chromatography on alumina using dibenzyl ether as solvent. Hence, following the separation of **2** and **3**, the fractions containing **3** were again submitted to vacuum trapping to isolate compound **3** in 63% yield. ^{1}H NMR analysis revealed a purity of 92% as 4% of mesityl oxide was detected, along with 4% of tetramethylethylene (TME).

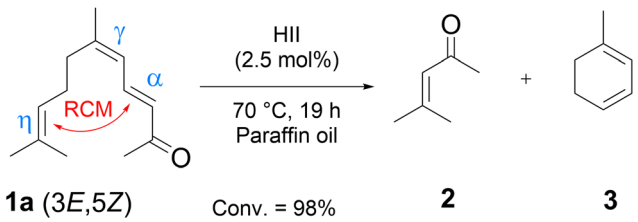
The other stereoisomer **1b** (3*E*,5*E*) was then subjected to the same experimental conditions, yielding, as could be anticipated from the results with commercial pseudoionone, a complex mixture of several compounds **4–6** and **8–10**. Of note, **2** and **3** were still observed but in low amounts (~8%). This very different reactivity between the two stereoisomers is well rationalized if one considers the possible conformations of these two compounds. As depicted in Fig. 4, when the C=C bond in position **5–6** (γ) presents a *Z*-configuration, the C3–C4 double bond (α) can be in the proximity of the prenyl double bond, whereas this is not possible with **1b**. Furthermore, the identification of **7** in the reaction mixture indicates the formation of **Ru-1** upon reaction with **1a** and **1b**, in which the bottom-side mechanism[49] places the prenyl-group in the *trans* position relative to the bulky NHC ligand, thus allowing RCM to occur. We cannot claim that this is the only pathway at play and that RCM does not occur following activation of the pre-catalyst at the prenyl-group (η double bond), but we did not detect the resulting product of such an activation by GC/MS, as we did with **7**.

Concerning the formation of products **5**, **6**, **8–10**, they can be easily interpreted by the various possibilities for the bimolecular self-metathesis of **1b**, each possibility potentially leading to four products depending on the regioselectivity of the interaction. For instance, **5** and **10** might result from the cross-metathesis of the γ and η carbon–carbon double bonds, whereas **6** and **8** might arise from the α and η C=C bonds, and **9** from α and γ C=C bonds. From the nature of the formed products, it appears that the α + α cross metathesis does not occur, as 3-hexene-2,5-dione was not detected.

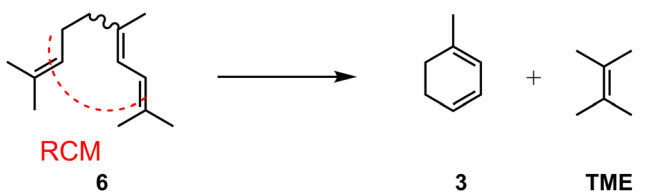
While the formation of **2** and **3** from **1a** can be rationalized, the formation of these two compounds from **1b** is not straightforward. This is also true if one considers that the commercial pseudoionone, composed of **1a**/**1b** in a 29/71 ratio (determined by ^{1}H NMR), provided 38% (GC yield) of **3** (*vide supra*), *i.e.*, a higher amount than theoretically expected.

As proposed above, the α + η double bond cross metathesis of **1b** leads to **8** and **6**, the latter possibly leading to **3** by RCM, which would also explain the formation of tetramethylethylene (TME) (Scheme 5). Note that the other regioselectivity, that of the α + η double bond cross-metathesis, would lead to **2** and a product of formula $C_{20}H_{30}O$ that was not detected by GC/MS, making this hypothesis unlikely.

In order to bring a rationalisation of these results, the composition of the reaction mixture using commercial pseudoionone was monitored *vs.* time by sampling and analysing aliquots with gas chromatography. As shown in Fig. 5, the two stereoisomers are not converted at similar rates, with **1a** being much more rapidly consumed. This is in line with the results obtained by Behr during the metathesis of *cis*- and *trans*-ocimene.[25] Most importantly, following a quick and almost



Scheme 4 Metathesis transformation of **1a** (150 mg, 0.78 mmol).



Scheme 5 Possible pathway for the synthesis of **3** by the RCM of **6** with TME as a co-product.

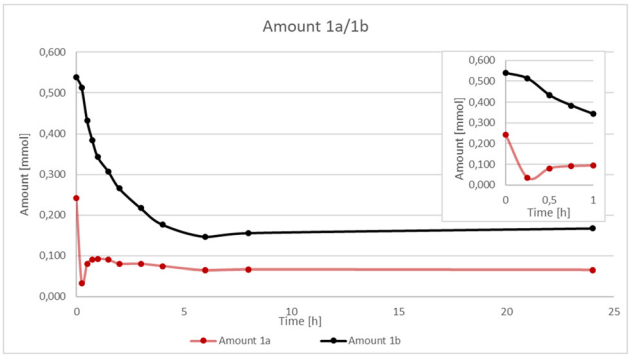


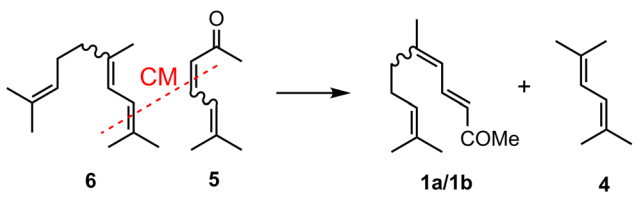
Fig. 5 Monitoring of the amount of **1a** and **1b** as a function of time. Zoomed-in image of the first hour is given at the top right corner.

full consumption of **1a** in the first minutes, its amount increased substantially to nearly ~33% of its initial amount before slowly decreasing (monitoring triplicated). If the reformation of **1a** during the reaction progress allows the formation of **3** in a higher amount than theoretically accessible, it is important to understand how this can occur, and several hypotheses can be proposed to explain this.

A first hypothesis would imply the formation of **1a** by secondary metathesis between products detected in the reaction mixture. For instance, **1a** and **1b** are accessible *via* cross-metathesis between compounds **5** and **6**, concomitantly explaining the formation of **4** (Scheme 6).

The isomerisation of **1b** into **1a** was also considered as a possible pathway accounting for the formation of **1a** during the reaction. However, if the isomerisation of vinyl carbenes, such as **Ru-2** (Fig. 6), is known, it concerns the selective isomerisation of the *Z*-isomer into the *E*-isomer,[50,51] *i.e.*, the opposite of what should occur in our case.

Furthermore, the rate of isomerisation of **1b** to **1a** should be higher than the rate of RCM from **1a** to account for the increase in the amount of **1a** following its drop to a minimal amount in the first 25 minutes (Fig. 5). Such a rate of isomerisation of **1b** should translate into a slope break in the conversion of **1b**, which is not visible in Fig. 5. For these reasons, we do not consider an isomerisation pathway as a realistic pathway accounting for the formation of **1a** during the reaction with commercial pseudoionone.



Scheme 6 Cross metathesis of **5** and **6**.

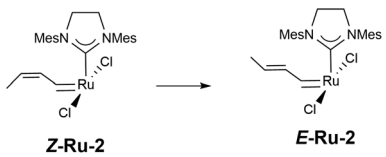
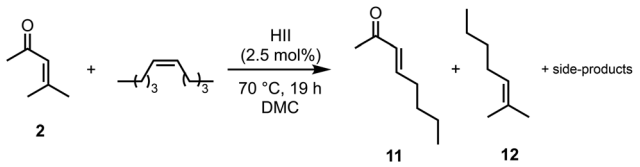


Fig. 6 Isomerisation of vinyl carbene.



Scheme 7 Cross metathesis of mesityl oxide **2** with (*Z*)-5-decene.

Finally, we turned our attention to the evolution of the amounts of **2** and **3** during the reaction. Theoretically, compounds **2** and **3** should be formed in equimolar amounts from **1a**, but we observed a higher amount of **3** as compared to **2**. Any loss of **2** due to evaporation was eliminated, and we propose that **2** could undergo metathesis transformation and thus be consumed once formed (secondary metathesis transformation). To check this hypothesis, **2** was reacted with (*Z*)-5-decene under our experimental conditions. As anticipated, this reaction delivered the cross-metathesis products **11** and **12**, along with some side metathesis products, resulting from double bond migration in (*Z*)-5-decene (Scheme 7). In an additional experiment, we have also disclosed that **2** does not react by self-metathesis. This reactivity of **2** accounts for the higher amount of **3** observed in our studies.

C. Conclusions

We synthesised and isolated the barely accessible 1-methyl-1,3-cyclohexadiene **3** from the biosourced pseudoionone. We have demonstrated that the stereoisomer **1a** (3*E*,5*Z*) in pseudoionone was the main precursor of **3** obtained by a ring-closing metathesis reaction. Consequently, with commercial pseudoionone consisting of a ≈30/70 mixture of **1a** and **1b** (3*E*,5*E*), respectively, **3** could be obtained in an isolated yield of 31%, corresponding to the theoretical yield. Alternatively, **3** could be produced in a very clean way and in high yield (63%) starting from pure **1a** obtained from the biosourced nerol. In this case, the only co-product of the reaction is mesityl oxide **2**, a known compound with well-identified applications. This work is a new contribution to the field of new bio-based chemicals. However, further improvements can be foreseen. Notably, due to the close boiling points of **2** and **3**, the purification of **3** was somehow difficult at laboratory scale, but this should not be an issue at a larger scale using an advanced distillation column with a large number of theoretical plates. Another way to explore is the selective transformation of commercial pseudoionone into **2** and **3**. This would require finding a catalyst and experimental conditions for the selective ring-closure of **1a** while leaving **1b** intact. This would also indirectly enable the isolation of pure unreacted **1b**.

Author contributions

A. Damiani: Investigation, methodology; L. Faber: Investigation, methodology, purification; B. Karim: Investigation; C. Bruneau: Project administration, supervision; W. A. Carvalho: Project administration; D. Mandelli: Conceptualisation, project administration, supervision; C. Fischmeister: Supervision, validation, writing original draft.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the SI.

Acknowledgements

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References

1 P. Gallezot, *ChemSusChem*, 2008, **1**, 734–737.
2 Y. Queneau and B. Han, *Innovation*, 2022, **3**, 100184.
3 Q. Hou, X. Qi, M. Zhen, H. Qian, Y. Nie, C. Bai, S. Zhang, X. Bai and M. Ju, *Green Chem.*, 2021, **23**, 119–231.
4 D. B. Pal, A. Singh and A. Bhatnagar, *Int. J. Hydrogen Energy*, 2022, **47**, 1461–1480.
5 J. A. Muldoon and B. G. Harvey, *ChemSusChem*, 2020, **13**, 5777–5807.
6 M. Christmann, *Angew. Chem., Int. Ed.*, 2010, **49**, 9580–9586.
7 A. Stepanyuk and A. Kirschning, *Beilstein J. Org. Chem.*, 2019, **15**, 2590–2602.
8 O. M. Ogba, N. C. Warner, D. J. O'Leary and R. H. Grubbs, *Chem. Soc. Rev.*, 2018, **47**, 4510–4544.
9 A. H. Hoveyda and A. R. Zhugralin, *Nature*, 2007, **450**, 243–251.
10 H. Bilel, N. Hamdi, F. Zagrouba, C. Fischmeister and C. Bruneau, *Green Chem.*, 2011, **13**, 1448.
11 D. C. Braddock and A. Matsuno, *Tetrahedron Lett.*, 2002, **43**, 3305–3308.
12 E. Borré, T. Dinh, F. Caijo, C. Crévisy and M. Mauduit, *Synthesis*, 2011, 2125–2130.
13 T. R. Hoye and H. Zhao, *Org. Lett.*, 1999, **1**, 1123–1125.
14 C. Bruneau, C. Fischmeister, D. Mandelli, W. A. Carvalho, E. N. dos Santos, P. H. Dixneuf and L. Sarmento Fernandes, *Catal. Sci. Technol.*, 2018, **8**, 3989–4004.
15 Z. J. Wang, W. R. Jackson and A. J. Robinson, *Org. Lett.*, 2013, **15**, 3006–3009.
16 L. Sarmento Fernandes, D. Mandelli, W. A. Carvalho, C. Fischmeister and C. Bruneau, *Catal. Commun.*, 2020, **135**, 105893.
17 L. Sarmento Fernandes, D. Mandelli, W. A. Carvalho, E. Caytan, C. Fischmeister and C. Bruneau, *Appl. Catal. A: Gen*, 2021, **623**, 118284.
18 A. Martínez, M. A. Tlenkopatchev, S. Gutiérrez, M. Burelo, J. Vargas and E. Jiménez-Regalado, *Curr. Org. Chem.*, 2019, **23**, 1356–1364.
19 V. K. Díez, C. R. Apesteguía and J. I. Di Cosimo, *J. Catal.*, 2006, **240**, 235–244.
20 K. Xing, K. You, D. Yin, Z. Yuan and L. Mao, *Catal. Commun.*, 2009, **11**, 236–239.
21 F. Zhou, H. Liu, Z. Wen, B. Zhang and G. Chen, *Ind. Eng. Chem. Res.*, 2018, **57**, 11288–11298.
22 L. Vieille-Petit, H. Clavier, A. Linden, S. Blumentritt, S. P. Nolan and R. Dorta, *Organometallics*, 2010, **29**, 775–788.
23 H. A. Meylemans, R. L. Quintana, B. R. Goldsmith and B. G. Harvey, *ChemSusChem*, 2011, **4**, 465–469.
24 K. A. Alexander, E. A. Paulhus, G. M. L. Lazarus and N. E. Leadbeater, *J. Organomet. Chem.*, 2016, **812**, 74–80.
25 A. Behr, L. Johnen, A. Wintzer, A. Gümüş, Ç. P. Neubert and L. Domke, *ChemCatChem*, 2016, **8**, 515–522.
26 J. M. Hidalgo Herrador, Z. Tišler, J. Kocík, J. Frątczak, I. Hradecká, R. Velvarská and H. De Paz Carmona, *Catalysts*, 2021, **11**, 1101.
27 S. Thotla, V. Agarwal and S. M. Mahajani, *Chem. Eng. Sci.*, 2007, **62**, 5567–5574.
28 M.-M. Xu, L. Yang, K. Tan, X. Chen, Q.-T. Lu, K. N. Houk and Q. Cai, *Nat. Catal.*, 2021, **4**, 892–900.
29 C. Liu and D. J. Burnell, *J. Am. Chem. Soc.*, 1997, **119**, 9584–9585.
30 M. Hatano, T. Sakamoto, T. Mizuno, Y. Goto and K. Ishihara, *J. Am. Chem. Soc.*, 2018, **140**, 16253–16263.
31 B. M. Trost, Z. Huang and G. M. Murhade, *Science*, 2018, **362**, 564–568.
32 R. Ding, J. Tian, H. H. P. van Erp and C. Reiter, *US* 2021/0309773A1, 2021.
33 J. Tian, X. Wei, J. Flood and V. Mhetar, *US* 2024/0304815A1, 2024.
34 D. T. Williamson, J. F. Elman, P. H. Madison, A. J. Pasquale and T. E. Long, *Macromolecules*, 2001, **34**, 2108–2114.
35 I. Natori, *Polym. J.*, 2003, **35**, 622–627.
36 S. Deng, M. K. Hassan, K. A. Mauritz and J. W. Mays, *Polymer*, 2015, **73**, 17–24.
37 K. Hong and J. W. Mays, *Macromolecules*, 2001, **34**, 782–786.
38 J. E. Baeckvall, S. E. Bystroem and R. E. Nordberg, *J. Org. Chem.*, 1984, **49**, 4619–4631.

39 M. Sellen, J. E. Baeckvall and P. Helquist, *J. Org. Chem.*, 1991, **56**, 835–839.
40 B. M. Trost and Z. Huang, *Angew. Chem., Int. Ed.*, 2019, **58**, 6396–6399.
41 M. Hatano, T. Sakamoto, T. Mizuno, Y. Goto and K. Ishihara, *J. Am. Chem. Soc.*, 2018, **140**, 16253–16263.
42 X. Miao, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *ChemSusChem*, 2008, **1**, 813–816.
43 C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.
44 I. W. Ashworth, D. J. Nelson and J. M. Percy, *Dalton Trans.*, 2013, **42**, 4110–4113.
45 K. Skowerski, J. Białecki, A. Tracz and T. K. Olszewski, *Green Chem.*, 2014, **16**, 1125–1130.
46 S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168–8179.
47 B. Wang and C. J. Forsyth, *Org. Lett.*, 2006, **8**, 5223–5226.
48 G. A. Abel, S. Viamajala, S. Varanasi and K. Yamamoto, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5703–5710.
49 A. Correa and L. Cavallo, *J. Am. Chem. Soc.*, 2006, **128**, 13352–13353.
50 S. T. Diver, *Coord. Chem. Rev.*, 2007, **251**, 671–701.
51 X. Niu, L. Gopal, M. P. Masingale, D. A. Braden, B. S. Hudson and M. B. Sponsler, *Organometallics*, 2000, **19**, 649–660.