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**Lauro lactam is an essential compound for the synthesis of polyamides and requires four separated steps for its industrial production, starting from cyclododecane. Here we show a one-pot synthesis of lauro lactam from cyclododecene, without intermediate purifications, in 66% yield. If desired, the intermediate cyclododecanone oxime can also be isolated, and the procedure is applicable for the production of capryl lactam.**

Lauro lactam **1** is the monomer used for the production of Nylon-12™,<sup>1</sup> which has a market that exceeds 100 000 tons per year and the sales account for >\$1.5 billion worldwide, expected to reach >\$2.0 billion by 2030. Therefore, efficient production of lauro lactam is essential to lower the price and the ecological footprint of Nylon-12™ in order to reach a sustainable global production for the coming years.

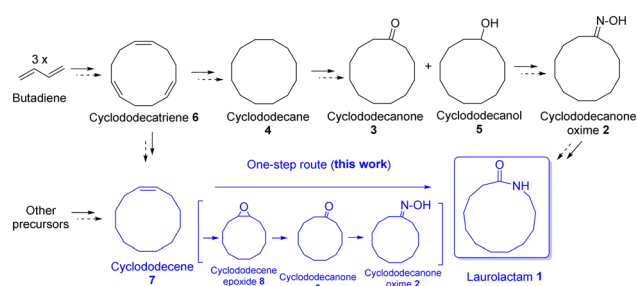
Fig. 1 shows the current industrial synthesis of lauro lactam **1**, which is based on the Beckmann rearrangement reaction of cyclododecanone oxime **2**, catalyzed by sulfuric acid. The purified cyclododecanone oxime **2** is in turn obtained by the oximation reaction of cyclododecanone **3**, and this ketone is produced in low yield (typically 5%) by a Co-catalyzed aerobic oxidation of cyclododecane **4**, resulting in a mixture of ketone **3** and alcohol **5**, which needs to be purified.<sup>2</sup> Ultimately, the starting cyclododecane **4** comes from cyclododecatriene **6**, obtained by the butadiene trimerization reaction. All these steps require individual purification processes to isolate the intermediates, since either the catalysts used, the excess of reactants or certain unwanted by-products lead to the partial or total inhibition of the next reaction along the established synthetic pathway. Therefore, it is not surprising that a high number of studies have been devoted during recent years to alleviating the issues associated to lauro lactam **1** production, with some of them trying to join some steps of the manufacture route.<sup>3</sup> However, the success of these approaches is somewhat

## One-pot synthesis of lauro lactam from cyclododecene and air

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limited due to the difficulties in obtaining pure cyclododecanone **3** during the direct oxidation of cyclododecane **4**.<sup>4</sup>

An alternative route for the introduction of the oxygen atom into the twelve-carbon atom cycle is the epoxidation of cyclododecene **7**, as also shown in Fig. 1. This mono-alkene can be obtained by selective hydrogenation of cyclododecatriene **6** (such as cyclododecane **4**) and, in contrast to the latter, other efficient synthetic routes are available for the production of cyclododecene **7**.<sup>5</sup> Thus, cyclododecene **7** can be considered as a potential starting material to synthesize lauro lactam **1**. Unfortunately, the second step for the synthesis of **1** from **7**, *i.e.* the epoxidation reaction to obtain epoxide **8**, has been mainly described with either *m*-chloroperbenzoic acid,<sup>6</sup> hydrogen peroxide<sup>7a</sup> (H<sub>2</sub>O<sub>2</sub>) and nitrous oxide<sup>7b</sup> N<sub>2</sub>O as oxidizing reagents, in excess, or in the presence of homogeneous catalysts based on tungsten, titanium or other transition metals.<sup>8</sup> These reaction conditions, in addition to the economic and environmental burden associated to the use of those epoxidating agents instead of air, are incompatible with the subsequent Meinwald rearrangement reaction to obtain cyclododecanone **3**, thus making a one-pot, single step reaction unfeasible<sup>3,9</sup> to achieve lauro lactam **1** from cyclododecene **7**.



**Fig. 1** The current industrial route for lauro lactam **1** synthesis, and the route herein reported. Solid arrows indicate a chemical transformation in a reactor and dashed arrows indicate the need for intermediate purification steps. Bracketed intermediates occur in a single reactor and do not need to be isolated.



At this point, we wondered if it would be possible to directly oxidize cyclododecene **7** to the epoxide **8** with air in good yields, without any catalyst,<sup>10</sup> and make this oxidizing system compatible for the next steps of the synthetic pathway, *i.e.*, the reactions of Meinwald transposition to ketone, and the oximation and transposition reactions to the lactam. In fact, the aerobic oxidation of cyclododecene **7** to the corresponding epoxide has been described, but using various catalysts, such as a combination of a Cu catalyst and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO),<sup>10b</sup> and with overoxidized by-products in all cases.<sup>11</sup> However, the selective epoxidation reaction of cyclododecene **7** occurs without a catalyst on the basis of our recent study on the aerobic epoxidation of alkyl alkenes<sup>12</sup> and also in, at least, another precedent for the aerobic epoxidation of cyclododecene<sup>13a</sup> and the related molecule cyclohexene.<sup>13b</sup> The epoxidation yield in the latter is very low (less than 10%) due to the excessive formation of over-oxygenated products,<sup>13c</sup> thus, we were positive in that our recent aerobic procedure,<sup>12</sup> which gives >90% of cyclododecene epoxide **8**, would be compatible with the designed cascade reaction. In our case, we make use of the alkene aggregation effect at high concentrations for better reactivity against oxygen,<sup>13d</sup> to avoid the use of high oxygen pressures and also the use of any solvent, and both improvements will make the next transposition reaction more compatible (see “Further comments on literature precedents” in the SI).

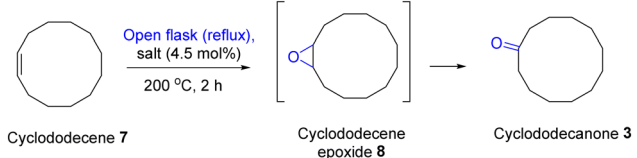
In our previous study,<sup>12</sup> we showed that the results for the uncatalyzed aerobic epoxidation reaction of cyclododecene **7** under neat oxygen (autoclave or bubbling) or just atmospheric air (open flask conditions) gave cyclododecene epoxide **8** as the major product with yields up to 80%. It is worthy to comment here that all reactions were carried out in glass reactors, avoiding any metal in contact with the reaction mixture, a key difference of our recently reported method compared to the previous literature.<sup>10</sup> Kinetic experiments show<sup>12</sup> that the epoxidation reaction smoothly occurs after an induction time, and that the selectivity towards product **8** is somewhat lost at high conversions and temperatures (Fig. S1), since ozone and oxygen free radicals are generated as by-products and start to break the epoxide. The formation of ozone during the reaction was checked by an *in situ* UV-vis reactivity test with indigo as a probe molecule, since the disappearance of the indigo absorption band at 604 nm together with the appearance of the band at 320 nm corresponding to the oxidation product with ozone is only observed when cyclododecene **7** was present in the reaction mixture.<sup>12</sup> Nevertheless, >99% selectivity to **8** is obtained in diluted air (66% yield of **8**, Fig. S2) which, strictly complies with the industrial requirement of operating under reaction conditions below the flammability limits of cyclododecene **7**.<sup>14</sup> The verification that O<sub>2</sub> was the source of O atoms for the epoxide during the reaction was carried out with isotopically labelled reactive experiments employing <sup>36</sup>O<sub>2</sub> instead of normal <sup>32</sup>O<sub>2</sub>, since the isotopically labelled epoxide product <sup>18</sup>O-**8** was found by both gas chromatography coupled with mass spectrometry (GC-MS) and Fourier-transformed infrared spectroscopy measurements (FT-IR),<sup>12</sup> with the

expected isotopic mass and infrared shift, respectively. Indeed, an open bottle of cyclododecene **7** in the laboratory can contain >5% of cyclododecene epoxide **8** and other overoxidized products (Fig. S3), in virtue of the natural oxidation with air during time, a feature barely commented in the literature. Kinetic experiments showed that cyclododecene **7** is reactive in either *cis* or *trans* form (the commercial sample employed here is 3:1 *cis:trans*), although the former seems somewhat more reactive (Fig. S4 and Table S1). In any case, it must be noted that the isomeric form of the epoxide **8** is in principle irrelevant for the next reaction during the one-pot synthesis, *i.e.* the formation of cyclododecanone **3**.

Cyclooctene **9** also gave the corresponding epoxide **10** in high yield (79%) under the optimized reaction conditions (Fig. S5) but, in contrast, cyclohexene **11** only gave a 4% of cyclohexene epoxide **12**, since most of the product comes from the classical allylic oxidation reaction, to give cyclohexenone **13**.<sup>15a</sup> These results reflect the subtle structure–reactivity relationship operating during the uncatalyzed aerobic oxidation of cyclic alkenes, apparently favouring the desired epoxidation reaction for macrocyclic alkenes such as cyclododecene **7** (see density functional theory, DFT, calculations ahead),<sup>15b</sup> something not studied in our previous study.<sup>12</sup> This result nicely fits the results obtained in a two-pot epoxidation experiment where neat cyclododecene **7** was treated with bubbled O<sub>2</sub> before the O<sub>2</sub> flow reaches a second flask with unreactive neat 1-tetradecene **14** (Fig. S6), to show that the terminal alkene **14** is epoxidized with air only after passing through cyclododecene **7**. This reactivity is explained by the higher electronic richness of the internal alkene **7** after aggregating in neat form (without any solvent),<sup>13d</sup> in order to activate O<sub>2</sub> for the epoxidation reaction (see the qualitative Fig. S7, investigated by DFT ahead).

Once we know that cyclododecene **7** is converted to cyclododecene epoxide **8** with just air and without any other additive, catalyst or solvent needed, we tested the one-pot formation of cyclododecanone **3** by a Meinwald transposition reaction. This reaction converts epoxides to ketones with either acidic catalysts or inorganic salts<sup>16</sup> which, in principle, could be compatible with our mild air-based epoxidation conditions. In this way, we would completely avoid the formation of cyclododecanol **5**, which inevitably occurs during the current cyclododecane **4** oxidation route. The results in Table 1 shows that a variety of simple and cheap salts are able to convert the *in situ* formed cyclododecene epoxide **8** into cyclododecanone **3**, in reasonable yields, particularly LiBr (entry 2), LiI (entry 3) and NaI (entry 6). The catalytic action of hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl, entry 8, industrially used for the oximation reaction)<sup>17</sup> is also remarkable since this will be the reagent for the next reaction step in the sequence, *i.e.* the oximation reaction and, indeed, a 32% of cyclododecanone oxime **2** is observed. Other salts gave poor selectivity to **3** (entries 1 and 5) or poor conversion (entries 4 and 7), the by-products being over-oxidated or oxidative breaking products. The addition of an active salt with poor selectivity (for example NaBr, entry 4) after the epoxidation reaction had been completed, *i.e.* as a sequential reaction, improved significantly



**Table 1** Results for the formation of cyclododecanone **3** after one-pot aerobic oxidation of cyclododecene **7** and Meinwald rearrangement of the *in situ* formed cyclododecene epoxide **8**, at 200 °C for 16 h, in the presence of different catalytic salts (4.5 mol%)


Entry	Salt	Conv. of 7 (%)	Yield (%)	
			8	3
1	LiCl	80	60	17
2	<b>LiBr</b>	<b>58</b>	<b>4</b>	<b>44 (85)</b>
3	<b>LiI</b>	<b>63</b>	5	<b>56</b>
4	NaCl	43	36	7
5 <sup>a</sup>	NaBr	82	18	20 (75)
6	<b>NaI</b>	72	<b>12</b>	<b>60</b>
7	KI	40	23	17
8 <sup>b</sup>	<b>NH<sub>2</sub>OH·HCl</b>	<b>62</b>	<b>0</b>	<b>28</b>

<sup>a</sup> In parentheses, result after adding the salt to the previously formed epoxide **8** (200 °C, 2 h). <sup>b</sup> The mass balance is completed with cyclododecanone oxime **2**.

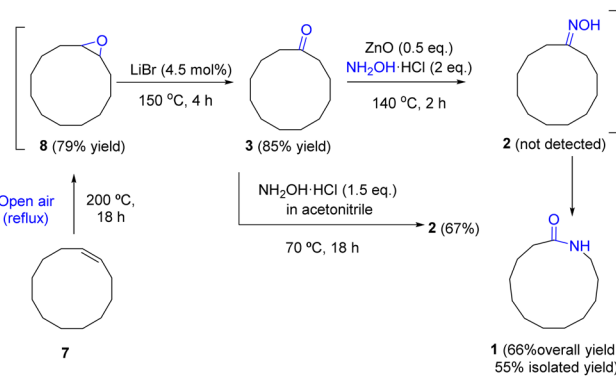
the conversion and selectivity (Table S2), to achieve a 75% of cyclododecanone **3**. These results indicate that the one-pot synthesis of cyclododecanone **3** from cyclododecene **7** can be achieved in good yields either by a cascade or sequential one-pot procedure.

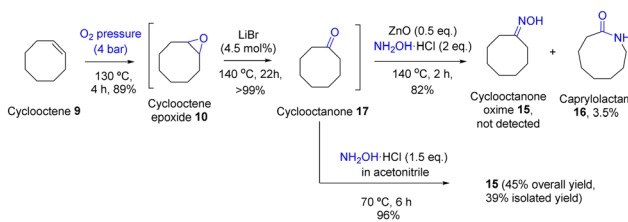
The next reactions to achieve lauro lactam **1** are the oximation of cyclododecanone **3** and the Beckmann transposition. As we have shown above,  $\text{NH}_2\text{OH}\cdot\text{HCl}$  can act as catalyst of the Meinwald transposition as a reagent of the oximation reaction. The participation of the Meinwald transposition in tandem reactions has been described,<sup>18a</sup> but not for the cascade reaction shown here. The Beckmann transposition is performed in the industry with sulfuric acid, resulting in a large amount of sulfated salts and wastewater as by-products of the reaction.<sup>18b</sup> However, milder acidic catalysts such as ZnO (ref. 18c) have been described to catalyze the reaction,<sup>18d,e</sup> including combinations of organic acids and inorganic salts.<sup>18b</sup> At this point, we thought that the addition of the simple metal salt ZnO will be enough to catalyze the Beckmann transposition with the help of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and the small amounts of carboxylic acids generated during the aerobic epoxidation stage. The result, shown in Fig. 2, confirms that a 66% yield of lauro lactam **1** is obtained from cyclododecene **7** when the reaction is run sequentially (Fig. S8 and S9) with a 55% of isolated yield starting from 5 mmol of cyclododecene **7**. If desired, cyclododecanone oxime **2** can be obtained in 67% yield if ZnO is not added and acetonitrile is employed as a solvent,<sup>19a</sup> and the reaction temperature is decreased.

The same sequential reaction protocol was then tested to achieve cyclooctanone oxime **15** and capryl lactam **16** from cyclooctene **9**, since the latter also reacts well during the uncatalyzed aerobic epoxidation reaction. The result in Fig. 3 shows that cyclooctanone oxime **15** can be obtained in an overall 45% yield (Fig. S10) with a 39% of isolated yield,

however, capryl lactam **16** was only obtained in <10% yield under these reaction conditions or other conditions tested (Fig. S11 and Table S3).

DFT calculations were performed in order to understand the reactive differences observed for the three different cyclic alkenes, the epoxide products, the classical allylic radical hydroperoxides<sup>19b,c</sup> and our recently proposed perepoxide intermediate products<sup>19d,e</sup> were computed, and there is an observable energetic compatibility between the frontier molecular orbitals (HOMO and LUMO) of the alkenes and those of the generated reactive oxygen species (Fig. S12). The double bond length and the corresponding natural population analysis (NPA) during the first interaction with the  $\text{O}_2$  molecule were then calculated (Fig. S13). It can be observed that the most polarized double bond is that of the eight-membered ring (with the greatest NPA charge difference), and it is also the one that undergoes the most significant perturbation in the presence of oxygen. The NPA

**Fig. 2** Result for the sequential one-pot reaction to achieve either lauro lactam **1** or cyclododecanone oxime **2** from cyclododecene **7**.



**Fig. 3** Result for the sequential one-pot reaction to achieve cyclooctanone oxime **15** or caprylolactam **16** from cyclooctene **9**. All yield results refer to gas chromatography (GC) yields, checked also by mass spectrometry (GC-MS) and using dodecane as an external standard.

spin charge analysis shows that the spin density is mainly localized on the oxygen (triplet), although in the case of cyclohexene **11**, it is slightly delocalized toward the alkene. Additionally, the system of two cyclododecene **7** molecules together, interacting through the alkene molecules in an orthogonal way, was computed (Fig. S14), and it was observed that the overlap of the HOMO and LUMO of both molecules causes a polarization of the electronic charge of the double bond, a fact that is consistent with the  $\pi$ - $\pi$  stacking effect considered as an activating mechanism. DFT calculations by superimposing the alkene bonds failed to converge to a reasonable energy, which supports that the model where the alkene molecules are interacting in an orthogonal way is more plausible. Two molecules of cyclohexene **11** were also computed and, in contrast to cyclododecene **7** and for a similar intermolecular distance, the double bonds of both molecules of **11** tend to repel each other, the double bond stretching is minimal and orbital interaction is observed only in the LUMO, while the polarization of the NPA charges remains negligible, which might lead to the failure of the catalyst-free aerobic epoxidation reaction. We have also performed new calculations with three instead of two alkene molecules, one molecule above and another below the double bond. However, all calculations failed so far, either with cyclododecene **7** or cyclohexene **11**, to converge to a reasonable energy, since the calculation is quite demanding. This work will be continued in the next studies.

To assess the efficiency and potential industrial applicability of the procedure, we calculated the *E* factor (kg of lauro lactam **1** per kg of waste generated).<sup>20</sup> The value for the present one-pot process compares very favorably with that of the current industrial method<sup>8b</sup> (1.7 vs. 16.2, respectively; Table S4), even if we start both procedures with cyclododecatriene (3.2 vs. 16.2), highlighting the efficiency and environmental advantage of the synthetic route reported herein.

## Conclusions

In summary, the synthesis of lauro lactam **1** from cyclododecene **7** has been achieved in good yield after a one-pot epoxidation, Meinwald rearrangement, oximation and Beckmann rearrangement sequential reaction. The procedure described here is performed in a single step, eliminating the purification of intermediates such as cyclododecanone **3** and its corresponding

oxime **2**, and the generation of residues such as sulfated salts and wastewater. It is true that the system here requires to prepare cyclododecene **7** from cyclododecatriene **6**, which is not trivial, since the conversion of the cyclic triene to the single alkene compound is challenging and initially a mixture with the diene is formed, requiring yet further purification steps; however, we think that an opportunity arises with our system here to prepare lauro lactam **1** in a more sustainable synthetic pathway.

## Author contributions

S. H.-A. performed the cascade reactions and the DFT calculations. S. R.-N. performed the cascade reactions. J. O.-M. designed the experiments and supervised the project. A. L.-P. designed the experiments and supervised the whole work. The manuscript has been written with contributions from all authors, which also interpreted all the experimental parts.

## Conflicts of interest

A Spanish patent (number P202431009) covering the cascade reaction here reported has been filed, with all the authors in this work appearing as co-inventors.

## Data availability

The datasets generated during and/or analysed during the current study are included in this published article (and its supplementary information (SI) files) or available from the corresponding author on reasonable request.

Supplementary information: experimental section, Tables S1–S5, Fig. S1–S17, compound characterization, computational cartesian coordinates and additional references. See DOI: <https://doi.org/10.1039/d5cy01180a>.

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