

## COMMUNICATION

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# Efficient epoxide isomerization within a self-assembled hexameric organic capsule†

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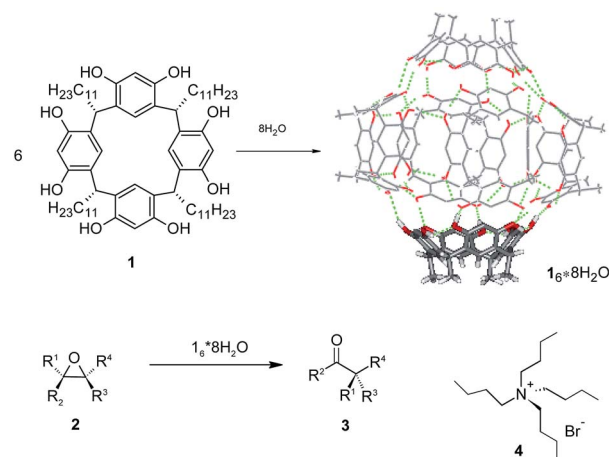
The isomerization of epoxides to the corresponding carbonyl compounds is efficiently catalyzed by the supramolecular organic nano-capsule formed by the self-assembly of six resorcin[4]arene units. The capsule provides a combination of weak Brønsted acidity and a suitable nano-environment that favors the metal-free isomerization reaction.

The epoxide isomerization known as Meinwald isomerization<sup>1</sup> is an atom efficient reaction that converts epoxides into carbonyl compounds of great synthetic interest.<sup>2</sup> The reaction can be accelerated by heterogeneous catalysts,<sup>3</sup> as well as homogeneous Brønsted acids and Lewis acids<sup>4</sup> with remarkable recent examples based on Pd<sup>5</sup> and Al<sup>6</sup> complexes. Alternatively, epoxides in the presence of basic species lead to the formation of allylic alcohols.<sup>7</sup> Isomerization reactions are very sensitive to the substitution pattern of the epoxide and this greatly effects the reactivity and selectivity of the reaction. Examples of stereospecific isomerizations of epoxides are indeed rare.<sup>8</sup> Apart from the above methods, at the best of our knowledge, no examples of purely organic catalysts for the epoxide to carbonyl compound isomerization are known.

Supramolecular catalysis<sup>9</sup> is a growing new cross-discipline<sup>10</sup> that aiming at mimicking enzymatic catalysis,<sup>11</sup> exploits the use of host structures to promote catalytic reactions. In the recent years self-assembled catalytic hosts have been introduced enabling co-encapsulation of more than one substrate as well as accommodation of metal catalysts.<sup>12</sup> Several efficient well defined catalytic host structures operate in water where the hydrophobic effect provides a good activation to the reaction favoring encapsulation of the substrate and subsequent stabilization of the transition state of the reaction. As long as supramolecular catalysis in organic media is concerned, the

seminal work of Rebek on the Diels Alder reaction within the hydrogen bonded dimeric softball capsule<sup>13</sup> paved the way to new larger supramolecular catalysts. In the recent years, the hexameric assembly  $1_6 \cdot (\text{H}_2\text{O})_8$  characterized by a very large cavity of about  $1375 \text{ \AA}^3$  (ref. 14) have been exploited to promote the stabilization of transition states of different classes of reactions<sup>15</sup> leading to substantial rate accelerations. In most cases it was demonstrated the importance of an accessible cavity in order to promote the catalytic reaction. In other recent examples, the capsule have been used as a nano-reactor to impart unique substrate<sup>16</sup> and product<sup>17</sup> selectivities and to reversibly control a photo-catalyst.<sup>18</sup>

Herein we present an example of metal free efficiently promoted epoxide isomerization mediated by the self-assembled organic supramolecular capsule of resorcin[4]arene  $1_6 \cdot (\text{H}_2\text{O})_8$  (Scheme 1). A peculiar role was played by the cavity of the capsule where the reaction takes place, mimicking the active sites of enzymes and observing typical inhibition of the catalytic activity in the presence of cationic competitive guests.<sup>19</sup>



**Scheme 1** Epoxide 2 isomerization reaction leading to the corresponding carbonyl compounds 3 in the presence of the capsule  $1_6 \cdot (\text{H}_2\text{O})_8$  and competitive guest tetrabutylammonium bromide 4.

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The isomerization reaction of styrene oxide **2a** as a model substrate was monitored over time by means  $^1\text{H}$  NMR and GC-MS analyses. As reported in Table 1 (entries 1 and 2) the reaction of **2a** in wet chloroform-d at  $60^\circ\text{C}$  for up to 18 h did not show evidence of the formation of isomerization or decomposition products. Only when catalytic amounts (7 mol%) of the capsule  $1_6\cdot(\text{H}_2\text{O})_8$  was added, the formation of the corresponding isomerized product phenylacetaldehyde **3a** in 69% yield was observed after 3 h at the same temperature, while quantitative formation of the product was achieved after 18 h (Table 1, entries 3 and 4 and Fig. 1C and D). A series of control experiments were carried out in order to ascertain the real role played by the capsule in the catalytic reaction. In order to exclude the direct involvement of the resorcinol moieties of **1** in the reaction, we repeated the tests as in Table 1 entry 1 replacing the hexameric capsule with 24 equivalents of 4-*n*-hexyl-resorcinol with respect to the original amount of capsule, observing almost no formation of **3a** (Table 1, entries 5 and 6 and Fig. 1F). This excludes the direct involvement of the resorcinol moieties in the catalytic isomerization reaction.

It is known that the hexameric  $1_6\cdot(\text{H}_2\text{O})_8$  behaves as a weak acid assembly with a  $\text{p}K_a$  of about 5.5, while the resorcinol moiety presents  $\text{p}K_a$  of 9.15. In order to mimic the same Brønsted acidity of the capsule,<sup>13f</sup> the reaction was repeated using acetic acid as catalyst (Table 1 entries 7 and 8) observing no formation of **3a** even after 18 h. This clearly indicates that it is not just the Brønsted acidity a key factor for the catalytic effect imparted by the supramolecular capsule. To further investigate the effect of the cavity of the capsule, the reaction of **2a** was followed in the presence of capsule with an excess of tetrabutylammonium tetrafluoroborate **4** as a competitive cationic guest for the cavity of the capsule.<sup>20</sup> The tetralkyl ammonium guest **4** was rapidly encapsulated<sup>20</sup> with concomitant inactivation of the catalytic activity (Table 1, entries 9 and 10 and Fig. 1E). All the reported data suggests that the reaction is favored by an accessible internal cavity of  $1_6\cdot(\text{H}_2\text{O})_8$ .

Table 1 Catalytic tests for the isomerization of styrene oxide **2a** to phenylacetaldehyde **3a**<sup>a</sup>

#	Time (h)	$1_6\cdot 8\text{H}_2\text{O}$	Additive	<b>3a</b> <sup>b</sup> (%)
1	4	—	—	0
2	18	—	—	0
3	3	+	—	69
4	18	+	—	>98
5 <sup>d</sup>	4	—	4- <i>n</i> -Hexyl-resorcinol	0
6 <sup>d</sup>	18	—	4- <i>n</i> -Hexyl-resorcinol	0
7 <sup>c</sup>	4	—	HAc	0
8 <sup>c</sup>	18	—	HAc	0
9 <sup>e</sup>	4	+	<b>4</b>	0
10 <sup>e</sup>	18	+	<b>4</b>	0

<sup>a</sup> [**1**] = 36 mM corresponding to 6 mM of capsule  $1_6\cdot 8\text{H}_2\text{O}$ , [**2a**] = 44 mM, water saturated chloroform-d 1.5 mL,  $T = 60^\circ\text{C}$ . +: presence; -: absence. <sup>b</sup> Determined by GC-MS. <sup>c</sup> [Acetic acid] = 35 mM. <sup>d</sup> [*n*-Hexyl-resorcinol] = 144 mM (24 eq. with respect to  $1_6\cdot 8\text{H}_2\text{O}$ ). <sup>e</sup> Tetrabutylammonium bromide [**4**] = 51 mM (>8 eq. with respect to the capsule).

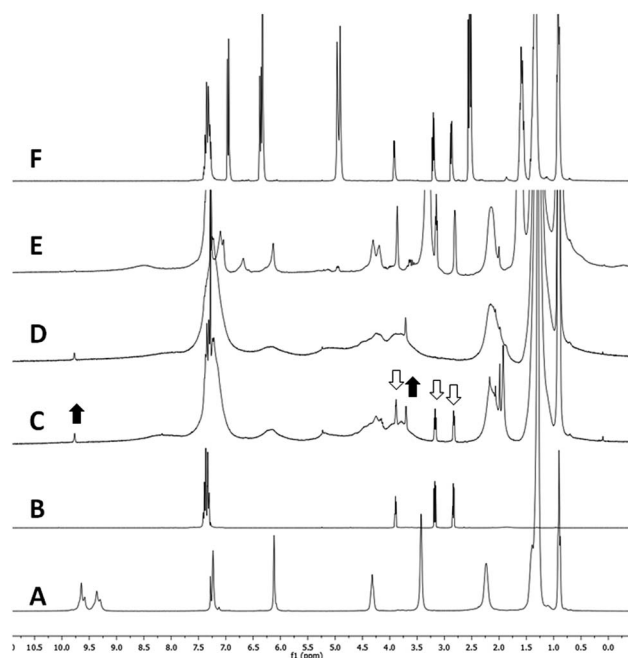


Fig. 1  $^1\text{H}$  NMR spectra in water saturated chloroform-d: (A)  $1_6\cdot 8\text{H}_2\text{O}$  (6 mM); (B) styrene oxide **2a** (44 mM); (C) styrene oxide **2a** (44 mM) and  $1_6\cdot 8\text{H}_2\text{O}$  (6 mM) after 3 at  $60^\circ\text{C}$ ; (D) styrene oxide **2a** (44 mM) and  $1_6\cdot 8\text{H}_2\text{O}$  (6 mM) after 18 at  $60^\circ\text{C}$ ; (E) styrene oxide **2a** (44 mM) and  $1_6\cdot 8\text{H}_2\text{O}$  (3 mM) and **4** (51 mM) after 18 h; (F) styrene oxide **2a** (44 mM) and 4-*n*-hexyl-resorcinol (144 mM) after 18 h  $60^\circ\text{C}$ .  $\uparrow$  Phenyl acetaldehyde,  $\downarrow$  styrene oxide.

The scope of the epoxide isomerization reaction was investigated applying the catalytic system to a wide range of terminal as well as internal epoxides (Table 2). It is widely accepted that the epoxide isomerization reaction occurs through the formation of the intermediate most stable carbocation species followed by migration of a residue leading to the final carbonyl compound.<sup>21</sup> While aliphatic epoxides did not react in the presence of the hexameric capsule due to high intrinsic stability,<sup>22</sup> aromatic epoxides showed good conversion for the *p*-Cl derivative **2b** as well as for the *m*-methoxy **2c** after 18 h reaction (Table 2, entries 1 and 3). Aromatic epoxides bearing a *m*-Cl **2d** or *m*-Br **2e** substituent led to 32% and 50% yield of the corresponding aliphatic aldehydes after 18 h and complete conversion after 32 h (Table 2, entries 3 and 4). The reactions showed to be sensitive to the electronic properties of the substrates,<sup>21</sup> in fact the electron poor *m*-NO<sub>2</sub> derivative **2f** turned out to be completely inactive while 2-methyl-2-phenyloxirane **2g** reacted spontaneously even without capsule (Table 2, entries 5 and 6). Larger substrates like *trans*-stilbene oxide **2h** and *trans*-stilbene oxide **2i** led to the same product **3h** showing a higher reactivity for the more compact *cis* isomer with respect to the *trans* derivative (Table 2, entries 7 and 8). An important substrate for isomerization reaction like  $\alpha$ -pinene oxide **2j** that can provide a wide range of possible isomers,<sup>23</sup> led to the formation of 82% yield of the campholenic aldehyde (Table 2 entry 9) together with minor isomeric by-products after only 4 h reaction. Another strained aliphatic epoxide like norbornene

Table 2 Epoxide isomerization reactions of **2b–2l** mediated by the capsule  $1_6 \cdot 8H_2O^d$ 

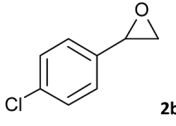
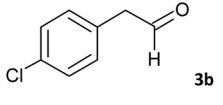
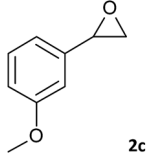
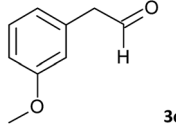
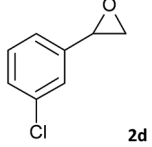
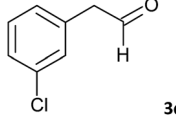
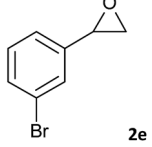
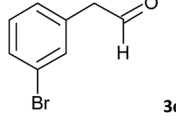
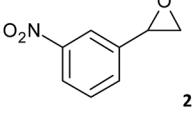
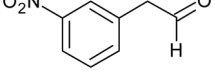
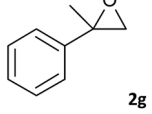
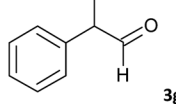
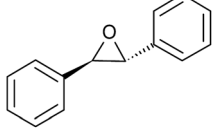
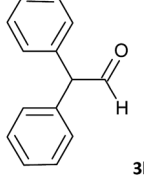
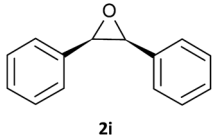
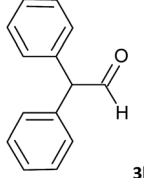
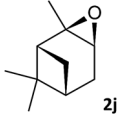
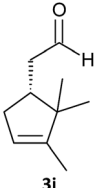
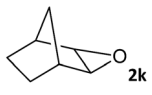
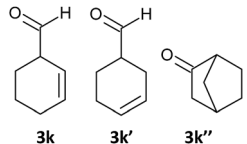
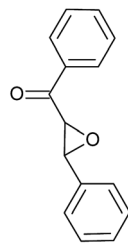
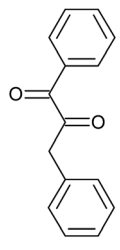
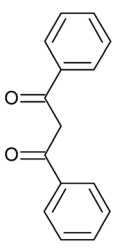
#	Substrate	Product	Yield <sup>b</sup> (%)
1			88 0 <sup>c</sup>
2			>98 0 <sup>c</sup>
3			32 (>98) <sup>d</sup> 0 <sup>c</sup>
4			50 (>98) <sup>d</sup> 0 <sup>c</sup>
5			0 0 <sup>c</sup>
6			>98 >98 <sup>c</sup>
7			84 0 <sup>c</sup>
8			>98 0 <sup>c</sup>
9			82 <sup>e,f</sup> 10 <sup>c,e</sup>
10			71 (56 : 27 : 17) 0 <sup>c</sup>

Table 2 (Contd.)

#	Substrate	Product	Yield <sup>b</sup> (%)
11		 	>98 (43 : 57) 6 <sup>c</sup> (78 : 22)

<sup>a</sup> Experimental conditions: [1] = 36 mM corresponding to 6 mM of capsule  $1_6 \cdot 8H_2O$ ; epoxide [2b–2l] = 44 mM, water saturated chloroform-d 1.5 mL,  $T = 60^\circ C$ ; time = 18 h. <sup>b</sup> Determined by GC-MS. <sup>c</sup> Reaction in the presence of [4] = 51 mM. <sup>d</sup> 32 h. <sup>e</sup> 4 h. <sup>f</sup> 18% of by-products.

oxide **2k** turned out to be less reactive in the presence of the supramolecular capsule, forming the corresponding isomerization products,<sup>24</sup> two aldehydes characterized by a different position of a cyclohexene unit (**3k** and **3k'**) and one bicyclic ketone **3k''**, in overall 71% yield (Table 2, entry 10). At last, an epoxide derived by *trans*-chalcone was investigated in the presence of the capsule leading to the formation of an  $\alpha$  and a  $\beta$  diphenyl propanone product in good yields (Table 2 entry 11).

In all the above cases, except for **2g**, the reactions with the capsule turned out to be extremely inactivated when carried out in the presence of the competitive tetrabutylammonium guest **4** as a clear indication of the reaction taking place within the cavity. The latter can accommodate about 6–8 chloroform molecules or a different combination of these with the epoxide substrate, in all cases in agreement with the typical packing coefficient observed for host–guests systems in solution.<sup>25</sup>

## Conclusions

In conclusion, we described an example of supramolecular catalysis where catalytic amounts of the hexameric self-assembled capsule  $1_6 \cdot 8H_2O$  promoted the isomerization of terminal and internal epoxides to the corresponding carbonyl compounds. The supramolecular capsule provides a suitable combination of weak Brønsted acidity together with a nano-environment within the cavity of the capsule that stabilize the formation of intermediate cationic species thus favouring the epoxide isomerization. Moreover, the inactivation of the reaction by addition of a competitive cationic ammonium guest for the self-assembled capsule clearly speaks for the occurrence of the reaction within the cavity of the organocatalyst, thus mimicking the active site of an enzyme.<sup>15</sup> It is worth to note that an example of a recombinant enzyme from *Pseudomonas putida* S12 that selectively promote the isomerization of epoxides to the corresponding aldehydes exist and is specifically active towards

aromatic epoxides.<sup>26</sup> This class of epoxides are intrinsically more active and the electronic properties of the aromatic residue affect heavily the activity. The catalytic effect observed with the hexameric capsule  $1_6 \cdot 8H_2O$  as a purely organocatalyst share some properties with the enzyme, albeit with reduced turnover which is due to the lower specificity of the supramolecular capsule compared to enzymes.

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