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The Ru(porphyrin)CO-catalyzed addition of aryl azides to styrenes to afford *N*-aryl aziridines was successfully performed for the first time in mesoreactors under continuous flow conditions. Mesofluidic technology allowed for a rapid screening of different parameters and a quick identification of the optimized reaction conditions.

Aziridines are valuable compounds largely employed as key starting materials for the synthesis of a plethora of nitrogen-containing molecules.<sup>1</sup> Among the different available synthetic strategies,<sup>2</sup> the metal-catalyzed addition of nitrenes to olefins represents one of the most popular and established methodologies for the preparation of aziridines.<sup>3</sup> In order to optimize the process sustainability, the selection of a convenient nitrene source is crucial. Thus, organic azides (RN<sub>3</sub>)<sup>4</sup> are largely used thanks to their high atom efficiency resulting in the formation of eco-friendly N<sub>2</sub> as the sole by-product of nitrene transfer reactions. Organic azide-based aziridinations are well catalyzed by several classes of metal transition catalysts and efficient stereoselective synthetic protocols have also been developed.<sup>5</sup>

However, the high reactivity that turns aziridines into excellent building blocks for further synthetic elaboration, on the other hand, makes these valuable compounds rather hazardous reagents to handle; a limited exposure to this class of compounds is therefore highly desirable. Furthermore, the synthesis and manipulation of azides are delicate processes, due to their inherent propensity for vigorous decomposition.

We felt that continuous flow methodologies<sup>6</sup> could provide a positive solution to some of the above mentioned issues to pave the way for a more widespread application of the metal-catalyzed synthesis of aziridines. In the last few years, flow chemistry technologies have become very popular in the synthesis of organic molecules,<sup>7</sup> including complex

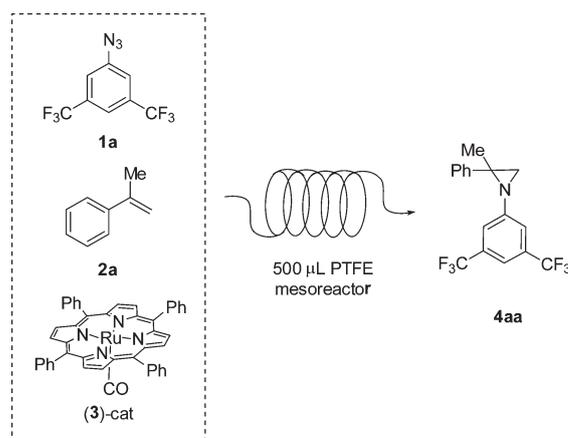
## Synthesis in mesoreactors: Ru(porphyrin)CO-catalyzed aziridination of olefins under continuous flow conditions†

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natural products<sup>8</sup> or Active Pharmaceutical Ingredients (APIs).<sup>9</sup> The attractive features of continuous processes are short reaction times, improved reagent mixing as well as mass and heat transfer. Safer handling of hazardous reagents or very reactive intermediates may also be positively addressed.

The synthesis of aziridines by flow chemistry techniques is largely underdeveloped, as evidenced by the scarce number of publications;<sup>10</sup> notably, as far as we know, examples of catalytic aziridinations in micro- or mesoreactors have never been reported. Considering that some of us have extensively studied nitrene transfer reactions promoted by ruthenium porphyrin complexes from both the experimental<sup>11</sup> and theoretical point of view,<sup>12</sup> we decided to investigate the Ru(porphyrin)CO-catalyzed aziridination of styrenes by aryl azides in mesoreactors under continuous flow conditions in an attempt to develop a simple, efficient and safe synthesis of aziridines.<sup>13</sup>

In a preliminary experiment, the reaction between 3,5-bis(trifluoromethyl)phenyl azide **1a** and  $\alpha$ -methylstyrene **2a**



**Scheme 1** Reaction between azide **1a** and  $\alpha$ -methylstyrene **2a** promoted by [Ru(TPP)(CO)] catalyst **3** in a continuous-flow system, using a 500  $\mu$ L PTFE mesoreactor.

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promoted by [Ru(TPP)(CO)] (TPP = dianion of tetraphenyl porphyrin) **3** was studied (Scheme 1).

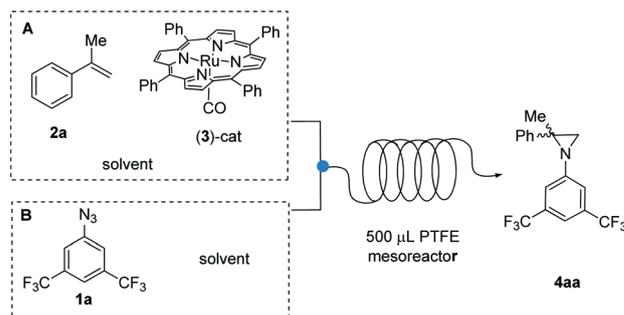
The reaction was conducted in a mesoreactor made of commercially available PTFE tubing (inner diameter 0.58 mm, length 189 cm, total volume 500  $\mu$ L) that was coiled in a bundle and immersed in a preheated oil bath. A New Era NE 300 syringe pump equipped with one Hamilton gastight 10 mL syringe was used in order to feed the reagents into the mesoreactor. Conversions and yields were determined by GC using biphenyl as the internal standard (see the ESI† for further details). A few selected results are reported in Table 1.

As initial conditions, a catalyst/azide/olefin ratio = 1 : 50 : 250 and a 0.2 M solution of azide **1a** in dry benzene were chosen in order to reproduce the batch conditions.<sup>11</sup> From previous work, it is known that refluxing benzene (typically 30 mL for a standard reaction procedure) was necessary in order to achieve high azide conversions, so the reactions were run at 90 °C. A small amount of 3,5-bis(trifluoromethyl)aniline (usually less than 3%) was detected as a by-product, in agreement with literature reports.<sup>11</sup> No product **4aa** was formed when working at room temperature for short reaction times.

Results of this initial screening are reported in Table 1. For short residence times, a low conversion was recorded for the catalytic reaction in benzene (entries 1–2, Table 1); a good yield of product **4aa** (85%) was obtained only by running the reaction for 60 min. It is interesting to note that changing the concentration of azide **1a** and olefin **2a** without modifying their stoichiometric ratios (0.2 M azide, olefin/azide/catalyst = 250 : 50 : 1) does not affect the yield of aziridine **4aa** appreciably (entry 2 vs. 4, Table 1). During all experiments, no clogging problems were encountered, but after 24 h, 11.4% of aziridine **4aa** was detected in the feeding syringe.

$\alpha$ -Methylstyrene **2a** was then used as the reaction solvent, but no improvements were obtained (entries 5 and 6, Table 1) at 90 °C, while a higher conversion was detected at 120 °C (entry 7, Table 1). Using a 0.2 M solution of azide **1a** yielded product **4aa** with no substantial improvement; however, we noted a high tendency of catalyst **3** to crystallize inside the feeding syringe.

On the basis of these preliminary results, we decided to change the feeding system by splitting the addition of the reactants into two different syringes (Scheme 2). A New Era NE



**Scheme 2** Reaction between azide **1a** and  $\alpha$ -methylstyrene **2a** promoted by [Ru(TPP)(CO)] catalyst **3** in a two-syringe continuous-flow system, using a 500  $\mu$ L PTFE mesoreactor.

300 syringe pump equipped with two Hamilton gastight 2.5 mL syringes was used to feed the reagents into the microreactor through a T-junction (syringe A: [Ru(TPP)(CO)] **3** dissolved in  $\alpha$ -methylstyrene **2a**;† syringe B: azide **1a** and biphenyl as the internal NMR standard dissolved in  $\alpha$ -methylstyrene **2a**). For convenience, 0.2 M solution of azide **1a** was used; selected results are reported in Table 2.

Running the reaction in  $\alpha$ -methylstyrene **2a** as the solvent had a beneficial effect on the reaction course in flow, resulting in higher azide conversions and in turn higher aziridine yields (entries 1–4 vs. entries 5–7, Table 2). In benzene, aziridine **4aa** was obtained in 27% yield after 30 min residence time, while the reaction run for the same time in  $\alpha$ -methylstyrene **2a** achieved 75.9% yield of the desired product **4aa**; the reaction selectivity was comparable in both cases (compare entries 3 and 7 of Table 2). Note that the replacement of benzene with  $\alpha$ -methylstyrene **2a** has a beneficial effect in terms of reaction eco-compatibility. In fact, solvent-free reactions are cleaner especially when the substrate, used as the reaction solvent, can be recycled in a continuous flow process.

Raising the temperature from 90 to 120 °C earned higher aziridine yields in short reaction times (entries 8–10, Table 2); **4aa** was produced in 95% yield after 10 min only and in almost a quantitative yield after 30 min residence time. Again, comparable selectivities were obtained in the examined cases.

**Table 1** Reaction between azide **1a** and  $\alpha$ -methylstyrene **2a** promoted by [Ru(TPP)(CO)] catalyst **3** in a one-syringe flow system, using a 500  $\mu$ L PTFE mesoreactor

Entry	[Azide] <sup>a</sup> (M)	Solvent	Residence time (min)	Temp (°C)	Conversion of <b>1a</b> <sup>b,c</sup> (%)	Yield of <b>4aa</b> <sup>b,d</sup> (%)
1	0.02	Benzene	10	90	49.4	39.7
2	0.02	Benzene	30	90	62.8	46.6
3	0.02	Benzene	60	90	89.3	84.7
4	0.2	Benzene	30	90	59.9	51.7
5	0.02	$\alpha$ -Me-styrene	5	90	44.1	41.9
6	0.02	$\alpha$ -Me-styrene	30	90	55.3	40.9
7	0.02	$\alpha$ -Me-styrene	5	120	54.8	41.6
8	0.2	$\alpha$ -Me-styrene	5	120	39.9	32.1

<sup>a</sup> Molarity values correspond to the effective concentration inside the microreactor. <sup>b</sup> Monitored by GC using biphenyl as the internal standard.

<sup>c</sup> Calculated as mmol of consumed **1a** per mmol of starting **1a**. <sup>d</sup> Calculated as mmol of **4aa** per mmol of **1a**.



**Table 2** Reaction between azide **1a** and  $\alpha$ -methylstyrene **2a** promoted by [Ru(TPP)(CO)] catalyst **3** in a two-syringe flow system, using a 500  $\mu$ L PTFE mesoreactor and  $\alpha$ -methylstyrene as the solvent

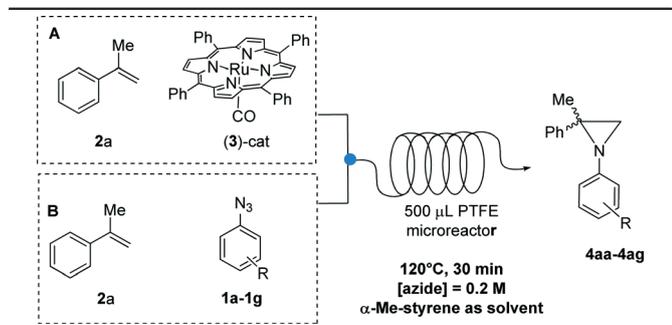
Entry	Solvent	Residence time (min)	Temp ( $^{\circ}$ C)	Conversion of <b>1a</b> <sup>a</sup> (%)	Selectivity of <b>4aa</b> <sup>b</sup> (%)	Yield of <b>4aa</b> (%)
1	Benzene	5	90	12.4	77.4	9.6
2	Benzene	10	90	19.1	91.1	17.4
3	Benzene	30	90	31.7	85.5	27.1
4	Benzene	60	90	57.8	51.5	29.8
5	$\alpha$ -Me-styrene	5	90	68.8	86.8	59.7
6	$\alpha$ -Me-styrene	10	90	66.8	85.5	57.1
7	$\alpha$ -Me-styrene	30	90	89.0	85.3	75.9
8	$\alpha$ -Me-styrene	5	120	90.6	96.7	87.6
9	$\alpha$ -Me-styrene	10	120	97.7	97.4	95.1
10	$\alpha$ -Me-styrene	30	120	98.9	99.1	98.0

<sup>a</sup> Monitored by GC using biphenyl as the internal standard. <sup>b</sup> Calculated as (mmol of aziridine)/(mmol of azide – mmol of azide residue)  $\times$  100.

Having identified the best reaction parameters and feeding mode, the scope of the ruthenium-catalyzed aziridination was studied; the reactivity of different aryl azides **1a–1g** was investigated in the reaction with  $\alpha$ -methylstyrene **2a** (Table 3).

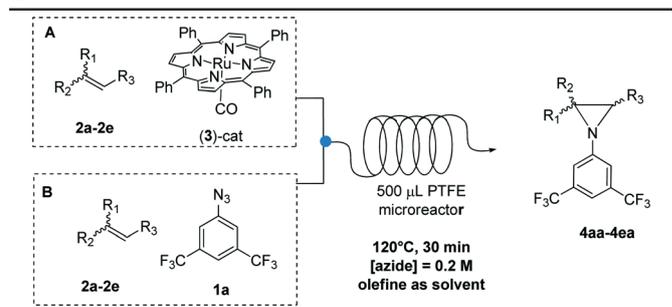
Aziridines **4aa–4ag** were all obtained in a selectivity higher than 80% in 30 min residence time. For very reactive azides **1a** and **1f**, bearing strongly electron-withdrawing groups, the selectivity was almost quantitative (entries 1 and 6, Table 3). The results were comparable to those reported in the literature.<sup>11</sup>

We then focused our attention on the study of the aziridination reaction of different olefins **2a–2e** by 3,5-bis(trifluoromethyl)phenyl azide **1a** (Table 4). As expected, styrene gave the desired product **4ba** in quantitative yield (entry 2, Table 4). 4-Br-styrene proved to be less reactive, affording

**Table 3** Aziridination reactions of  $\alpha$ -methylstyrene **2a** by different aryl azides **1a–1g** catalyzed by **3** in a two-syringe flow system, using a 500  $\mu$ L PTFE mesoreactor

Entry	R	Azide residue <sup>a</sup> (%)	Product yield <sup>a,b</sup> (%)	Selectivity <sup>c</sup>
1	3,5-(CF <sub>3</sub> ) <sub>2</sub>	1.1	<b>4aa</b> 98	99
2	4-Cl	34	<b>4ab</b> 53	80
3	4-NO <sub>2</sub>	22	<b>4ac</b> 64	82
4	4-CF <sub>3</sub>	16	<b>4ad</b> 73	87
5	4-Br	20	<b>4ae</b> 63	80
6	3,5-Cl <sub>2</sub>	5	<b>4af</b> 93	98
7	4-CN	31	<b>4ag</b> 55	80

<sup>a</sup> Determined by <sup>1</sup>H NMR. <sup>b</sup> Calculated as (mmol of aziridine)/(mmol of azide)  $\times$  100. <sup>c</sup> Calculated as (mmol of aziridine)/(mmol of azide – mmol of azide residue)  $\times$  100.

**Table 4** Aziridination of different olefins **2a–2e** by 3,5-bis(trifluoromethyl)phenyl azide **1a** catalyzed by **3** in a two-syringe flow system and a 500  $\mu$ L PTFE mesoreactor

Entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Azide residue (%)	Product yield (%)	Selectivity <sup>c</sup>
1	CH <sub>3</sub>	Ph	H	1.1 <sup>a</sup>	<b>4aa</b> 98 <sup>a</sup>	99
2	H	Ph	H	3.4 <sup>a</sup>	<b>4ba</b> 90.1 <sup>a</sup>	93
3	H	4-Br-C <sub>6</sub> H <sub>5</sub>	H	2.9 <sup>a</sup>	<b>4ca</b> 62 <sup>a</sup>	64
4	H	Ph	CH <sub>3</sub>	1.5 <sup>b</sup>	<b>4da</b> 55 <sup>b,d</sup>	44
5	Ph	Ph	H	2.0 <sup>b</sup>	<b>4ea</b> 89 <sup>b</sup>	91

<sup>a</sup> Monitored by GC using biphenyl as the internal standard. <sup>b</sup> Calculated by NMR using 3,5-dinitrotoluene as the internal standard. <sup>c</sup> Calculated as (mmol of aziridine)/(mmol of azide – mmol of azide residue)  $\times$  100. <sup>d</sup> Product was obtained as a 9:1 mixture of *cis*: *trans* isomers.

aziridine **4ca** in 64% yield (entry 3, Table 4).  $\beta$ -Methylstyrene gave the corresponding product **4da** as a mixture of 9:1 *cis*: *trans* isomers in a quantitative conversion but only 55% yield (entry 4, Table 4). 1,1-Diphenylethylene afforded aziridine **4ea** in 98% yield (entry 5, Table 4). All the results were in agreement with literature data and with the reaction mechanism that favors terminal olefins with respect to internal olefins.<sup>11</sup>

It is noteworthy that the productivity $\S$  of the flask process for the synthesis of aziridine **4aa** calculated according to literature conditions (90  $^{\circ}$ C, 30 min, 97% yield)<sup>11</sup> was 98 617; a comparable productivity, 87 600 h<sup>-1</sup>, was obtained for the flow process, working at 120  $^{\circ}$ C for 5 min residence time only (88% yield). We also report in Table 5 the space-time yields for the two processes, measured as [mass (product)/(vol(reactor)  $\times$  reaction time) expressed as kg m<sup>-3</sup> s<sup>-1</sup>; this



**Table 5** Flask vs. flow comparison for aziridination of  $\alpha$ -methylstyrene **2a** by azide **1a** promoted by [Ru(PPP)(CO)] catalyst **3**

Entry	Reactor	Time (min)	Temp (°C)	Yield (%)	Reactor volume (mL)	Space-time yield <sup>a</sup>
1 <sup>b</sup>	Flask	30	90	97	30	$3.78 \times 10^{-3}$
2 <sup>c</sup>	Flask	5	120	99	30	$23.17 \times 10^{-3}$
3 <sup>d</sup>	PTFE	5	120	87.6	0.5	$20.16 \times 10^{-3}$
4 <sup>d</sup>	PTFE	10	120	95.1	0.5	$10.95 \times 10^{-3}$
5 <sup>d</sup>	PTFE	30	120	98.0	0.5	$3.75 \times 10^{-3}$

<sup>a</sup> Measured as [mass (product)/(vol(reactor) × reaction time)] expressed as kg m<sup>-3</sup> s<sup>-1</sup>. <sup>b</sup> See ref. 11. <sup>c</sup> Run in  $\alpha$ -methylstyrene as the reaction solvent. <sup>d</sup> This work.

value takes into account the volume of the reactor (or the flask) used to perform the reaction.

Data show that the two systems give comparable space-time yields (entries 2 and 3, Table 5). However, the flow process has the advantage of performing reactions in compact devices and small reaction volumes rather than in batch systems with larger reaction volumes.

## Conclusions

In conclusion, the addition of aryl azides to styrenes for the synthesis of *N*-aryl aziridines was successfully accomplished in a PTFE mesoreactor under continuous-flow conditions, in the presence of a ruthenium porphyrin-based catalyst. Yields and selectivities of the flow process favorably compare with those of the batch reaction, with the undeniable advantage of operating with smaller reaction volumes. The procedure without solvent becomes even more appealing when functionalized, more expensive styrene derivatives are used, with the possibility of recycling the substrate in a continuous flow process. The methodology opens new opportunities for a very convenient synthesis of functionalized aziridines with a safe, fast and experimentally simple procedure.

## Acknowledgements

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## Notes and references

‡ Catalyst **3** was heated until completely dissolved (see the ESI†).

§ For the definition of productivity and numbers, see the ESI†

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