

# Batch vs. Flow Photochemistry: A Revealing Comparison of Yields and Productivities

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**Abstract:** The use of flow photochemistry and its apparent superiority over batch has been reported by a number of groups in recent years. In order to rigorously determine whether flow does indeed have an advantage over batch, a broad range of synthetic photochemical transformations were optimized in both reactor modes and their yields and productivities compared. Perhaps surprisingly, yields were essentially identical in all comparative cases. Even more revealing was the observation that the productivity of flow reactors varied very little to that of their batch counterparts when the key reaction parameters were matched. Those with a single-layer of FEP had an average productivity 20% lower than that of batch whilst 3-layer reactors were 20% more productive. Finally, the utility of flow chemistry was demonstrated in the scale-up of the ring opening reaction of a potentially explosive [1.1.1] propellane with butane-2,3-dione.

## Introduction

In the last ten years the use of flow chemistry in organic synthesis has increased dramatically, and is now rapidly being established as a routine tool for mainstream synthesis.<sup>[1]-[6]</sup> Flow techniques have also been applied to synthetic organic photochemistry on a variety of platforms.<sup>[9],[10]</sup> In 2005 Booker-Milburn and Berry reported a practical flow reactor for general lab based synthetic photochemistry.<sup>[11]-[13]</sup> This employed a reactor of flexible, UV transparent FEP (fluorinated ethylene propylene) tubing wrapped closely around a UV emitting source (Figure 1a). The surface area and proximity of the photolysate to the UV source ensured effective irradiation of large volumes of solution minimizing transmission vs. distance constraints, resulting in the production of 20-500 g of photochemical products in 24 h. Precise regulation of flow rate enabled residence time to be controlled in cases where over-irradiation of evolving product is a problem.<sup>[14]-[16]</sup> Recently a second generation reactor has enabled use of air cooled low-pressure 36 W lamps in conjunction with FEP tubing,<sup>[16]-[18]</sup> with the advantage of allowing controlled irradiation at selected wavelengths centered around 254, 312 and 365 nm by simply exchanging lamps (Figure 1b).

The FEP reactor concept has now been used and adapted for a number of reactions, resulting in the synthesis of a wide range of complex, photochemically derived products.<sup>[19]-[28]</sup> Perhaps the most striking of these has been the use of an FEP flow reactor in the scaled-up continuous synthesis of the frontline anti-malarial drug artemisinin by Seeberger and Lévesque.<sup>[29],[30]</sup>

Many groups have now reported the advantages of flow photochemistry over previously reported batch results.<sup>[9],[10]</sup> Whilst it is true that scale-up has now been clearly demonstrated in flow and there is a real safety advantage when irradiating large volumes of flammable solvents, flow photochemistry involves a considerable equipment investment compared to the simplicity of a conventional batch reactor. On scale-up the increased path length of larger batch reactors theoretically suffer from the constraints imposed by the Beer-Lambert law (e.g. longer reaction times/photo-degradation), nevertheless huge photochemical industrial processes have been developed in batch. For example the Toray process for the synthesis of cyclohexanone oxime (Nylon 6 production) is a semi-continuous photochemical batch process that in 1976 had a worldwide production capacity of 160,000 tonne/pa.<sup>[31]</sup>

Faced with this conflicting picture, is it possible that batch limitations in photochemistry are not as great as feared and the superiority of flow is yet to be proven unequivocally? With many readily available bespoke and commercially available reactor choices, today's first-time photochemistry user may well ask the question "which is better, batch or flow?" With this in mind we embarked on an investigation and careful comparison of batch vs. flow reactor performance for a variety of different photochemical reactions. This study would prove for the first time whether photochemical flow reactors are more or less productive under the same time period of an optimized batch process when both are exposed to the same amount of UV light.

## Results and Discussion

Attempting to compare batch and flow photo-reactors is not straightforward, as encapsulating the light efficiently in flow is more challenging due to the non-planar surface of the tubing, gaps between the tubing and absorption of light by the FEP. To enable fair comparison between reactors, all reactions were performed keeping parameters of concentration, lamp power, and distance of photolysate from the UV source as identical as possible. Although it is commonplace in flow chemistry to use residence times (*ie* reactor volume  $\div$  flow rate) for comparison with batch reaction times, in photochemistry this often leads to incorrect conclusions (*vide infra*) regarding various reaction outcomes.<sup>[9]</sup> Consequently, both modes were optimized independently under the above reaction parameters and their yields and critically, productivities compared at the end time point obtained for the batch process.

Table 1 summarizes the extensive data collected on twelve different cycloaddition and rearrangement reactions. Perhaps the most strikingly obvious feature is the similarity in isolated yields between batch and flow, which in most cases are essentially identical. After extensive optimization of each reaction it also became clear that the productivity of the flow reactor differed to that of the batch reactor by a relatively small amount. As in previous studies,<sup>[11]</sup> the number of layers of FEP had a significant effect. For example in entry 1, although the yields of **3**<sup>[32]</sup> were the same, the productivity was 50% higher for a 3-layer compared to 1-layer system. This was due to the more effective capture of light in the 3-layer system, enabling a faster flow rate (3 mL/min) and the isolation of 62.7 g of **3** in a single 22 h run. Conversely, it was clear that the 1-layer system was less effective at capturing light thus reflecting its lower productivity compared to batch (5.70 g vs. 6.56 g in 3 h). For this reason all subsequent reactions studied with a 400 W lamp utilized the 3-layer system. The other maleimide cycloadditions (entries 2-4)<sup>[11],[32]-[33]</sup> proceeded in a similar fashion and the desired [2+2] cycloaddition adducts were obtained in near identical yields for both batch and flow reactions but with slightly greater productivity levels for flow.

Entry 5 proved to be very interesting. It was found that the absorption of amino maleimide **10** is red shifted with respect to the parent maleimide, similar to the methoxy maleimides we have previously studied.<sup>[34],[35]</sup> This amino maleimide chromophore had a  $\lambda_{\max}$  centered at 350 nm, ideally suited to irradiation with 36 W UVA lamps (Figure 2). Under flow conditions this intramolecular [2+2] cycloaddition was an exceptional performer with a productivity of 12.69 g/100 min at 80% isolated yield. The absorption was so strong, and the efficiency of the reaction so high, that it could be run at a flow rate of 16 mL/min using two 36 W lamps in series, enabling the production of 40 g of tricyclic product **11** in a 5 h run. However, when it came to comparing the batch process using the same low-pressure 36 W lamp we were faced with the problem that the lamp was too long to be fully immersed in a 400 mL batch immersion well and only half of the lamp could be utilized. When this batch irradiation was carried out in this way it gave an optimized 77% isolated yield of the tricyclic product at a productivity of 3.11 g/100 min. On face value this appears to be a quarter as productive as the flow result for the same time period. However, when the four-fold power difference is factored in the results between batch and flow are remarkably similar at the 100 min batch end point. With the 36 W low-pressure lamps a 3-layer version was not investigated as the longer length of the lamps (40 cm) would require a large amount of FEP, leading to an excessive reactor volume (~300 mL).

Entry 6 describes the known<sup>[36]-[38]</sup> intramolecular cycloaddition of dieneone **12** to caged diketone **13** with a single 36 W UVA lamp in flow. The batch reaction was conducted using ~50% immersion of the lamp. Optimized yields were again very similar and it was found that the batch reaction was approximately 20% more productive once the power difference had been accounted for. Interestingly, unlike the flow reactor, for this example the batch reactor suffered from foul-up over time and required cleaning (base bath) between runs. Recently Loubiere<sup>[39]</sup> and co-workers described a chemical engineering analysis of this reaction in a microcapillary flow reactor and also concluded that in this case productivity was higher in batch.

The intramolecular [2+2] cycloaddition<sup>[40]</sup> of pyrrole **14** (Entry 7) provided an example of the use of a 36 W UVC lamp at 254 nm, which was also conducted with 50% lamp immersion. Once power correction had been applied this also displayed the same trend as entry 6. Although the yield and power corrected productivity in batch was higher, by using a 3-lamp system in flow we were able to produce 29.2 g of **15** in a single 21 h run (*cf.* 10.06 g/7 h). To process the same 5 L solution of substrate **14** in batch would be impractical. The cycloaddition was also carried out with a 125 W medium pressure lamp through a quartz filter (see SI Figure S14; 69%, 0.57 g/2 h). Over the course of 7 h this lamp could only produce about 2 g of **15**, the same as half a 36 W UVC lamp. This clearly demonstrates the superior efficiency of the low-pressure UVC emission over that of a medium pressure lamp.

The Paternò-Büchi reaction of benzaldehyde and dihydrofuran **16** (Entry 8) had previously been optimized in a detailed study by Griesbeck using a falling film reactor with a high power 3 kW XeCl excimer lamp (75%, 130 g, 14 h).<sup>[41]</sup> In our hands, scale-up under batch conditions at 0.3 M concentration gave a 67% isolated yield (14.05 g, 3 h) of oxetane **17** using a 400 W lamp. Under flow conditions an optimized 72% yield was obtained with a productivity of 20.52 g at the batch end point of 3 h. This represented an almost 50% increase in productivity for the flow reactor in this particular case.

Moving away from 4-membered ring formation we next studied the performance of the maleimide chromophore in the previously developed<sup>[42],[43]</sup> intramolecular [5+2] cycloaddition to azepines (entries 9 & 10). With dimethylmaleimide **18** the reactions were run at two different concentrations, the lower concentrations enabling a higher conversion to be obtained in a shorter reaction time. For this reaction, it was remarkable to observe identical yields for batch and flow, even with a 10-fold difference in concentration. However, in both cases flow conditions proved to be approximately 20% more productive than batch.

The [5+2] cycloaddition of dichloromaleimide **20** proved to be a very interesting example (Entry 10). Previously in batch this reaction had proved very sensitive using a 125 W lamp at 0.02 M, and the window between maximum conversion of starting material and over-irradiation of the sensitive product was very narrow.<sup>[9],[14]</sup> Consequently, we had previously never been able to perform this reaction on scales much greater than 0.5 g using batch apparatus. So it was to our surprise that when this reaction was performed at the much higher concentration of 0.1 M in batch (400 mL) with a 400 W lamp, we were able to follow the reaction over time without observing any noticeable product degradation (Figure 3).

In batch azepine formation progressed rapidly over the first 100 min or so to give an optimal conversion in the region of 60-70% (by NMR). Cessation of irradiation at this point gave a 62% isolated yield of pure azepine **21** with a productivity of 5.82 g/100 min. We found that the batch reaction could be irradiated for a total of 210 min allowing for the isolation of product in a record yield of 69%, albeit at a lower productivity. This product was also less pure; a tell-tale red colouration indicating photo-degradation from over-irradiation.

Two factors are likely at play here: firstly, at this higher concentration the sensitive product is more effectively 'screened' by the starting maleimide. Secondly, as the irradiation time is longer at higher concentration, the reaction was much easier to monitor by NMR, and therefore the point between maximum conversion and over-irradiation could be more accurately determined compared to our earlier studies. This example clearly illustrates the importance of matching substrate concentration with photon flux (lamp power) in batch reactions *i.e.* too much power risks product degradation and too little leads to slow and incomplete conversion. Performing the reaction in flow using a 3-layer system (0.1 M, 4.2 mL/min) resulted in essentially identical yield and productivity to batch (5.90 g/100 min, 60% yield).

Entry 11 describes an acetophenone-sensitized di- $\pi$ -methane rearrangement first reported by Edman.<sup>[44],[45]</sup> We found this reaction to be exceptionally efficient both in flow and in batch and actually struggled to identify its limits. For example this was run at a very high concentration of 0.6 M to give almost quantitative yields in both batch and flow, with the latter proving marginally more productive at the batch end time.

Entry 12 describes a reaction previously developed by us<sup>[17]</sup> involving the irradiation of pyrrole **24** to tricyclic aziridine **25** via a complex photochemical two-step process. As consistent with the rest of the 1-layer/36 W reactors used in this study, the yields between batch and flow were essentially identical, with a minor increase in batch productivity when the power correction was factored in.

Finally, we studied the scale-up of the photochemical ring opening of propellane **26** with butane-2,3-dione to diketone **28** which was previously described in batch<sup>[46],[47]</sup> (58%, 26.5 g, 8 h). After optimization in flow, this reaction proceeded in an identical 58% yield, but with greatly increased productivity to deliver 51.8 g of pure **28** in a single 70 min run (projected 1.07 kg/24 h). Due to the potentially explosive nature (see SI Figure S19) of **26** we declined to carry out a comparative batch reaction on the same scale. The ability to safely irradiate large quantities (1400 mL) of the potentially hazardous solution of **26** through a relatively small reactor (53 mL volume) represents a significant safety advance for this useful reaction (Scheme 1).

As mentioned previously residence times are commonly used in flow chemistry to assess the efficiency of a reactor. In our own experience with flow-photochemistry we have found residence time to be a less relevant parameter than productivity, especially when comparing batch and flow. For example, the data collected for the cycloaddition of **1** to **3**, can be used to compare residence time and productivity as metrics of the efficiency of a reactor. On residence time alone the Reactor 3 would appear to be superior *i.e.* 2x faster than Reactor 2 and 8 x faster than Reactor 1 in achieving the same maximum 68% yield. However, analysis of productivities shows this approach to be highly misleading as it is immediately apparent that the 3-layer reactor is superior for preparative chemistry (Table 2). For example, running the reaction in Reactor 2 for 22 h gave 63 g of isolated product **3**. In the same time period Reactor 3 would give approximately 40 g of product.

This highly rewarding study has uncovered a number of features of both batch and flow photochemistry for a wide variety of reactions. When comparing both modes at the same photolysate concentrations, UV lamp powers and wavelengths, three important and general trends are apparent:

- Yields for batch and flow reactors in synthetic photochemistry are essentially the same at full conversion.
- 3-layer FEP reactors have on average 20% higher productivity compared to the same batch end-point.
- 1-layer FEP reactors have on average 20% lower productivity compared to the same batch end-point.

It is straightforward to understand the lower productivity of a 1-layer FEP reactor compared to batch due to the shorter path lengths, gaps between channels, and the absorption of light by FEP. For example, in scenario A (Figure 4), light entering a tube would encounter some absorption by FEP polymer, before either exciting a substrate molecule or leaving the FEP tube. In scenario B, light could simply pass through the gaps between the FEP tubing. Overall, this would result in less efficient capture of photons in the 1-layer reactor compared to batch. Moving to the 3-layer system this reactor consistently exceeded the productivity of the batch reactor by an average of 20%. This enhancement over the 1-layer system reflects increased residence time due to the larger reactor volume and the resultant improvement in the capture of photons previously lost through gaps in the channels (scenario B). This leads to an increase in the effective path length, as any light leaving the inner layer would be able to penetrate the second and third layers. It is also interesting to compare the path length of the batch reactor (8.7 mm) with the 3-layer flow reactor. Although it is tempting to

suggest that the flow reactor path length is similar ( $3 \times 2.7 = 8.1$  mm) to batch, Figure 4 shows that due to the offset layering of the FEP tubing the effective path length is likely to be significantly less. Combining this with the expected absorption of FEP tubing, one might expect batch to be superior to even the 3-layer FEP reactor. Clearly, however this is not the case. At present the superior performance of the FEP reactor is not fully understood and may reflect more complicated factors such as different concentration gradients between tubes and possible light scattering effects affecting photon path lengths (Figure 4, C).

## Conclusions

In light of this study the answer to the question - "*which is better, batch or flow?*" - is a complex one, as we have shown that both modes can do the same chemistry in essentially identical yields and similar productivities for a range of reactions. Ultimately scale will likely dictate which reactor the user chooses.<sup>[48]</sup> For example, batch photochemical reactors are ideal for first time reactions (and users) due to lower cost, ease of operation, reaction monitoring and ease of optimization. To avoid over-irradiation in batch it is essential to match the power of the lamp with the concentration of substrate (e.g. entry 10). It is likely that in the past many poorly performing small scale batch reactions have been unnecessarily discounted due to over-irradiation with an unsuitably matched UV source. Batch reactors using 400 W lamps and 400 mL volume immersion wells are well suited for reactions up to 10-15 g scales, and in some cases even larger (e.g. entry 11). FEP flow reactors are ideal for producing products on scales of greater than 10 g in a single run, and for processing larger volumes safely and efficiently (e.g. 26 to 28, Scheme 1). FEP reactors are also ideal for irradiating large volumes of dilute solutions, which would be impractical in batch mode, especially when using large low-pressure lamps (e.g. Entries 5,7 & 12).

This study concludes that where productivity is concerned both batch and flow modes of irradiation are equally important in synthetic photochemistry. The choice of one mode over the other depends on what is required from a particular experiment. We hope that these observations will enable first time users of photochemistry to choose appropriately. Finally, this study highlights clearly that unless careful steps are taken to compare batch vs. flow under the most equitable conditions possible, then it is difficult to make meaningful conclusions between the two. This in turn risks leading to dogmatic assertions over the superiority of one mode over another. This study has been highly revealing and has helped overturn assumptions we have held over our own previous work in the area. Whilst these conclusions hold for the range of photoreactions described in this study, it is unclear whether similar outcomes would be observed for other types of reaction involving light e.g. photocatalysis, photooxygenation, SET etc. We hope similar studies in these areas and other non-photochemical areas of flow chemistry are carried out so that the field can blossom into a technique that is used in conjunction with established batch modes rather than attempt to compete against it.

## Experimental Section

A comprehensive account of all experimental details including supplementary figures and tables, full experimental procedures, analytical data, as well as copies of <sup>1</sup>H and <sup>13</sup>C NMR data, is provided in the supplementary information.

### General Details

Batch reactions were analysed over time by <sup>1</sup>H NMR using an internal standard (see SI for detail). The productivity of a batch reactor was then determined by the amount of product isolated over the reaction time. For short flow photochemistry runs at least one reactor volume was allowed to pass through the irradiated reactor (to achieve "steady-state") before photolysate was collected for a determined run time. For longer runs of several hours and beyond, the total photolysate was collected. In each case the product was isolated and purified and the amount obtained was then extrapolated up or down to match the batch end point.

*Batch Reactors* (Figure 1a) were standard immersion-well quartz reactors fitted with a Pyrex sleeve (36 mm o.d., 33 mm i.d.) that accommodate a 400 W medium pressure Hg-lamp and have a typical filled volume of 400 mL - that is the volume of photolysate that covers the whole length of the Hg-lamp. The reactor's effective path length was calculated to be approximately 8.7 mm. Cooling was provided by either mains water or by a glycol/water chilled circulator. Where monochromatic radiation was used, 36 W (40 cm) single ended PL-L lamps (254 or 365 nm) were inserted into the unfiltered quartz immersion well (*i.e.* no pyrex sleeve) resulting in approximately 50% immersion (see SI for exact power conversions in each case).

*400 W Flow Reactors* (Figure 1a) have been described previously by us<sup>[11]</sup> and involve 1-3 layers of FEP tubing (2.7 mm i.d., 3.1 mm o.d.) wrapped around a customized water or glycol cooled Pyrex immersion well (with sufficient tubing to cover the whole length of the Hg-lamp - approx. 15 cm) containing a 400 W medium pressure Hg lamp. Reactor Volumes: 45 mL (1-layer); 145 mL (3-layer).

*36 W Flow Reactors* (Figure 1b) have been described previously by us<sup>[17]</sup> and involve 1-layer of FEP tubing (2.7 mm i.d., 3.1 mm o.d.) wrapped around a custom quartz tube containing a low pressure 36 W single ended PL-L lamp (254 or 365 nm) cooled by air. Reactor Volume: 90 mL (1-layer).

## Acknowledgements

We thank Novartis (LDE), EPSRC EP/K006053/1 (PJK), EPSRC EP/L003325/1 (LDE), University of Bristol (JPK) for Postdoctoral funding, and the EPSRC Bristol Chemical Synthesis Doctoral Training Centre (EP/G036764/1), AstraZeneca, Syngenta for PhD studentship funding (KGM, MJR). We also thank P. Dinham, D. Mitchell & D. Tarling (University of Bristol) for reactor construction, and C. Heuberger (Novartis, Basel) for DSC analysis of **26**.

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**Figure 1. Batch and flow reactors used in this study.** (a) Comparison of the footprints of a 400 W medium pressure Hg lamp batch reactor and power supply (left) with equivalent 3-layer FEP flow reactor and peristaltic pump (right). (b) A triad of 1-layer FEP reactors customized for use with 40 cm 36 W low-pressure Hg lamps. This example depicts the use of 254 nm (UVC) lamps where 3-reactors have been daisy-chained together for increased productivity (see Table 1, entry 7).

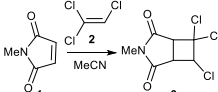
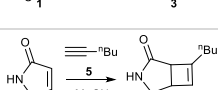
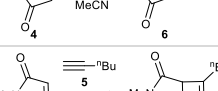
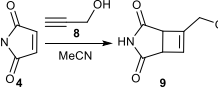
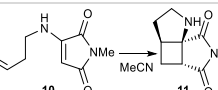
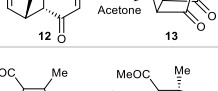
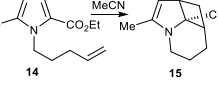

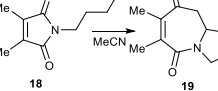
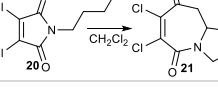
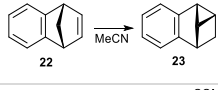
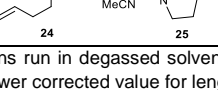





**Figure 2.** UV absorption of amino maleimide **10** overlaid with emission of 36 W UVA low-pressure lamp.

**Figure 3.** Batch [5+2] Photocycloaddition of Dichloromaleimide **20** monitored over time using <sup>1</sup>H NMR with 1,3,5-trimethoxy benzene as internal standard.

**Scheme 1.** Photochemical ring opening and reaction of propellane **26** with butane-2,3-dione in Flow

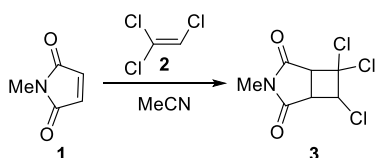
**Figure 4.** Light transmission scenarios through 1-layer and 3-layer FEP reactors

**Table 1.** Batch vs. Flow Yields and Productivities for a Variety of Photochemical Reactions

Entry	Lamp	Mode	Conditions <sup>a</sup>	Yield(%)	Productivity at batch end pt. (g)	Batch vs. Flow <sup>g</sup>	
1		400 W	Batch	0.096 M, 180 min	68	6.56	1/1.30
		400 W	Flow <sup>b</sup>	0.096 M, 3 mL/min	68	8.55	
		400 W	Flow <sup>c</sup>	0.096 M, 2 mL/min	68	5.70	
2		400 W	Batch	0.1 M, 120 min	67	4.77	1/1.24
		400 W	Flow <sup>b</sup>	0.1 M, 4 mL/min	68	5.90	
3		400 W	Batch	0.1 M, 80 min	56	4.32	1/1.12
		400 W	Flow <sup>b</sup>	0.1 M, 6 mL/min	52	4.82	
4		400 W	Batch	0.1 M, 120 min	65	4.0	1/1.18
		400 W	Flow <sup>b</sup>	0.1, 4 mL/min	64	4.70	
5		1 x 36 W UVA	Batch	0.05 M, 100 min	77	3.11 [12.44] <sup>f</sup>	1/1.02
		2 x 36 W UVA	Flow <sup>c</sup>	0.055 M, 16 mL/min	80	12.69	
6		1 x 36 W UVA	Batch	0.1 M, 105 min	80	7.09 [13.10] <sup>f</sup>	1.22/1
		1 x 36 W UVA	Flow <sup>c</sup>	0.1 M, 7.5 mL/min	77	10.70	
7		1 x 36 W UVC	Batch	0.02 M, 7 h	84	2.10 [4.20] <sup>f</sup>	1.19/1
		1 x 36 W UVC	Flow <sup>c</sup>	0.02 M, 2 mL/min	75	3.54	
		3 x 36 W UVC	Flow <sup>c</sup>	0.03 M, 4 mL/min	72	10.06	
8		400 W	Batch	0.3 M, 3 h	67	14.05	1/1.46
		400 W	Flow <sup>b</sup>	0.3 M, 3 mL/min	72	20.52	
9		400 W	Batch	0.1 M, 4 h	63	4.88	1/1.20
		400 W	Flow <sup>b</sup>	0.1 M, 2 mL/min	63	5.87	
		400 W	Batch	0.02 M, 2 h	76	1.18	
		400 W	Flow <sup>b</sup>	0.02 M, 4 mL/min	77	1.43	
10		400 W	Batch	0.1 M, 100 min	62	5.82	1/1.02
		400 W	Flow <sup>b</sup>	0.1 M, 4.2 mL/min	60	5.90	
11 <sup>d</sup>		400 W	Batch	0.6 M, 135 min	90	30.70	1/1.10
		400 W	Flow <sup>b</sup>	0.6 M, 3.3 mL/min	89	33.83	
12		1 x 36 W UVC	Batch	0.02 M, 310 min	49	0.80 [2.0] <sup>f</sup>	1.08/1
		1 x 36 W UVC	Flow <sup>c</sup>	0.02 M, 3.1 mL/min	46	1.86	

<sup>a</sup>All reactions run in degassed solvents; <sup>b</sup>3-layers of FEP, flow direction outer layer to inner; <sup>c</sup>1-layer of FEP; <sup>d</sup>50 mol% acetophenone sensitizer; <sup>e</sup>Parentheses indicate power corrected value for length of the lamp effectively covered (see SI for detail); <sup>g</sup>Ratio of productivities; All products are racemic.

**Table 2.** Comparison of Residence Time vs. Productivity in three different reactors



Reactor	Type	Volume	Flow rate	Residence time	Productivity	Yield
1	Batch	418 mL	n/a	180 min	2.20 g/h	68%
2	3-layer	145 mL	3 mL/min	48 min	2.85 g/h	68%
3	1-layer	45 mL	2 mL/min	23 min	1.90 g/h	68%

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#### **Batch vs. Flow Photochemistry: A Revealing Comparison of Yields and Productivities**

**Spot the difference:** By careful matching of reaction parameters the performance of 13-different photochemical reactions were compared in both batch and flow reactors. Surprisingly, the yields obtained in the different reactor modes were essentially identical. Similarly, the productivity differences between the two reactor modes, under the same time scales, were relatively small.

**Keywords:** Flow photochemistry • Batch reactor • Cycloaddition • Rearrangement • Scale-up