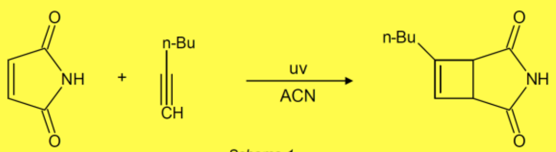
Application Note 47:

[2+2] Photocycloaddition with wavelength specific low pressure mercury lamps

Produced by Vapourtec

Abstract

This application note uses the photochemical reaction explored in application note 36, the photocycloaddition of maleimide and 1-hexyne, to explore the performance of Vapourtec's new low pressure mercury lamps. For this reaction the low pressure lamps are used in place of the medium pressure lamp with filters. Three low pressure mercury lamps are tested, each with a specific and very narrow wavelength emission band.



Scheme 1

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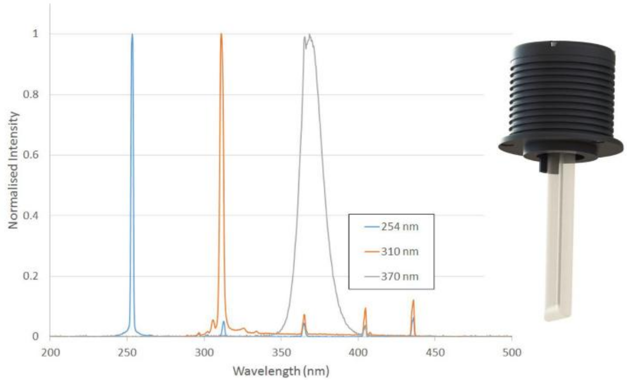
Background

This application note demonstrates the use of low pressure mercury lamps with varying wavelengths and investigates the rate of reaction in the photocycloaddition of maleimide and 1-hexyne using three different wavelengths, 254 nm, 310 nm and 370 nm.

As with previous app notes, photochemical reactions in flow chemistry provides a huge range of advantages over batch conditions including:

- Uniform and constant exposure
- Controllable exposure times
- Continual removal of products which may compete in absorbance
- Controllable parameters, such as temperature and reaction time

Previously, in app note 36, a medium pressure mercury lamp was used with a quartz filter and chiller to reduce the reaction temperature to 30 °C, as the medium pressure lamp generates a large amount of heat. Vapourtec's new, efficient, low pressure mercury lamps have approximately one fifth of the intensity of a medium pressure mercury lamp, have very specific wavelength emission and generate very little heat (resulting temperature rise <1 °C above ambient). Graph 1 shows the wavelength emissions of each lamp tested.



Graph 1 wavelength emission of the 3 low pressure mercury lamps tested

Method

System Setup

The flow reactor was set up using the Vapourtec E-series as shown in figure 1.

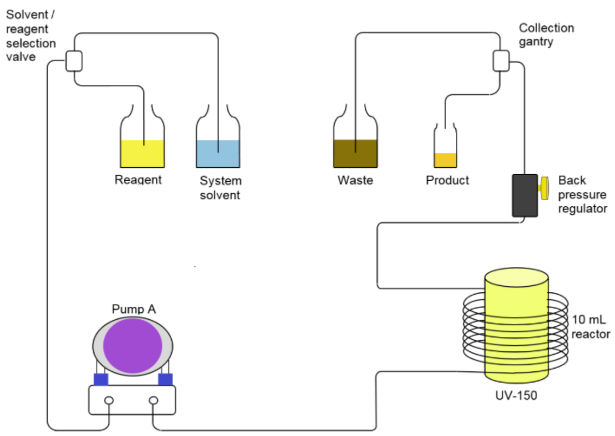


Figure 1

Pressure was controlled by a variable back pressure regulator (BPR). The elution outflow was collected via the waste/collection switching valve.

Pump Tubing

The E-Series is fitted with three high performance V-3 peristaltic pumps and features a fluoropolymer tube as its core. The pumps feature more than one different tube type to ensure the largest range in compatibility of solvents. Therefore the correct selection of tubing is crucial for any given reaction.

A table showing recommended tube type compatibility with a wide selection of solvents, acids and bases is available within the E-Series manual and also built into the user interface software. It is important to note, each V-3 pump can achieve a maximum of 10 mL/min. The solvent was acetonitrile, so either tubing can be used. For this experiment, red tubing was used.

Reagents

All reagents and solvents used were purchased from Sigma-Aldrich.

System Parameters

System solvent:	Acetonitrile
Solution A:	0.02 M Maleimide (1.0eq), 1-hexyne (1.5 eq) in ACN
UV Light Sources:	Low pressure mercury lamp (254 nm, 310 nm and 370 nm)
Flow rate A:	1 – 4 mL/min
Reactor volume:	10 ml FEP reactor
Reactor temperature:	30 °C
Back pressure regulator:	Atmospheric pressure

The reaction process followed the sequence of steps listed below:

1. *Prepping the system*
   The system was primed by running the system solvent through the pump and reactor and all connections were set up and checked.
2. *Product pumping and collection*
   The reactions were run automatically using flow control software on the E-Series. After prepping the system, the parameters were set for the reaction and allowed to run until completed. Using flow control software a desired amount of product was collected from the steady state using the automatic collection gantry valve.
3. *Analysis*
   A small amount of the resulting product was heavily diluted in acetonitrile and analyzed by HPLC using an H_2O/ACN mobile phase. The degree of conversion was assessed by the appropriate integration peaks.

Results and discussion

From previous spectroscopic data obtained from app note 36, the reaction between maleimide and 1-hexyne absorbs light very strongly below 300 nm, strongly between 300 and 340 nm, and weakly above 340 nm.

Each low pressure mercury lamp was tested at the same conditions and the conversion and throughput were compared. The results are shown in table 1.

Table 1

Wavelength (nm)	Residence time (min)	Concentration (M)	Conversion (%)	Throughput (g/h)
370	5	0.02	11.3	0.049
310	5	0.02	84.0	0.361
254	5	0.02	95.2	0.410
310	10	0.02	95.6	0.206
254	2.5	0.02	71.0	0.610

254 nm was absorbed the strongest and gave the fastest rate of reaction. 310 nm did give a good conversion, but the absorption was weaker than the 254 nm. 370 nm was barely absorbed at all and resulted in poor conversion and very poor throughput. These results with the specific wavelength low pressure mercury lamp correlates with the spectroscopic data from app note 36.

Conclusion

This brief application note shows that low pressure mercury lamps are an effective light source and can match the specificity of LED's but in addition offer wavelengths below 365 nm combined with multi-watt radiant power that is not currently available at with LEDs. As with LEDs, the low pressure mercury lamps do not require any filters and do not require a chiller to prevent an increased reaction temperature due to excess heat generation.