

From the Solar Production of Chemicals to Microphotochemical Synthesis

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Over the last decades, the call for sustainable and environmentally friendly technologies has led to an increasing interest in Green Chemistry.¹ Among the known green chemical approaches, organic photochemistry can serve as a valuable application since light is regarded as a clean and traceless reagent.² Light can also be controlled with a ‘flick of a switch’. Despite this advantage, however, synthetic organic photochemistry has been widely ignored by the chemical industry.³

Solar Photochemistry – ‘Back to the Roofs’

One of the main reasons for the neglect of photochemistry as a production method is the high energy demand of most artificial light sources. Scharf and co-workers have recently used concentrated sunlight as an alternative and ‘freely available’ light source for the solar production of selected fine chemicals.⁴ This concept leads back to the beginnings of organic photochemistry in the late 19th century (and thus ‘back to the roofs’) where sunlight was the only available source of radiation.⁵

Over the last decade, we have realized a number of laboratory- to large-scale solarchemical photoacylation and photooxygenation reactions in sunlight using solar reactors (Fig. 1).⁶⁻⁹ All reactions yielded valuable commodity chemicals and gave complete conversions (>95%) and excellent chemical yields after relatively short illumination times.



Fig. 1 – PROPHIS (back) and CPC (front) reactors at the German Aerospace Centre (DLR) in Cologne, Germany.

The photosensitized oxygenation (or Schenck ene reaction) of citronellol and its subsequent reduction (Fig. 2), for example, were studied as a model of an industrially relevant process.^{6,8} This transformation is currently performed industrially on a >100 t/a scale by Symrise in Germany using artificial light sources. Acid mediated cyclization of the regioisomer **2b** gives the important fragrance rose oxide. Due to its obvious industrial importance, this photoreaction has become a prototype for solar photochemical comparison studies.

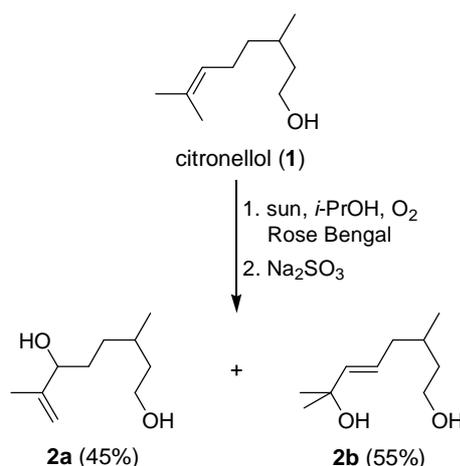


Fig. 2 – Photooxygenation of citronellol (1).

For the solar reactions in the PROPHIS loop, the sensitizer Rose Bengal was selected since it shows a favorable absorption of up to 600 nm in the solar spectrum. The solvent methanol from the industrial process was successfully replaced by the less hazardous isopropanol. Using these parameters, 31-44 mol of **1** were converted within 3 hours of solar illumination. This reaction was also studied in less advanced reactor systems and gave comparable results.

Microphotochemistry – ‘Photochemistry on a chip’

Microreactor technology is currently an area of rapid growth and a number of chemical trans-

formations have been realized on micro to pilot production scales.¹⁰ Likewise, microphotochemistry, i.e. photochemistry in microstructured reactors, has emerged as a new photochemical R&D synthesis tool.¹¹ The thin layers within the microreactor channel allow extensive penetration of the solution by light. In addition, the short residence time within the (flow-through) reactors avoid undesired follow-up reactions or decompositions. These features, together with the typically small reaction scales, make micro(photo)reactions interesting for Green Chemistry.

We have thus studied a series of homogeneous and heterogeneous photoreactions in a dwell device or a falling-film microreactor to evaluate the potential of microphotochemistry.¹²⁻¹⁵ We have also designed a novel LED-driven microchip (Fig. 3) and successfully applied it to isopropanol additions to furanones (Fig. 4).^{13,14} All results were compared to analogous experiments in conventional batch reactors. In all cases examined, the reactions performed in the chosen microreactors gave higher conversions or yields thus proving the superiority of the microphotochemistry concept.

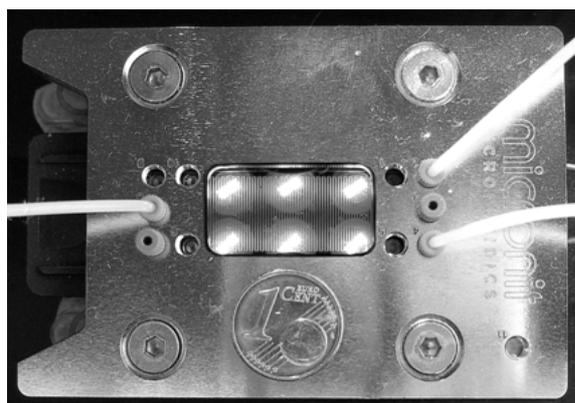


Fig. 3 – Micronit microchip with 6 × 365 nm LED array.

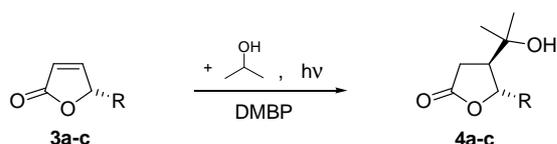


Fig. 4 – Isopropanol addition to furanones (3).

Major disadvantages of commercially available microreactors are, however, the fixed length of the reaction channel and the single-channel design. Although numbering-up can be achieved using an array of microreactors,¹⁰ this strategy causes significant investment costs. Flexible capillaries represent a cost-efficient alternative. We have thus designed and tested a simple continuous flow dual microcapillary tower.^{13,15} The tower design also enables reactions in parallel capillaries and a 10-

capillary twin-tower has been constructed and tested for process optimization and library synthesis.

Conclusions

In conclusion, photochemistry can serve as a powerful and green technology for both, the production of established commodity chemicals and the synthesis of novel compound libraries. Solar photochemistry allows for ‘scale up’ (production), whereas microphotochemistry allows for ‘scale down’ (R&D).

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