Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Electronic Supplementary Information

A greener process for flow C-H chlorination of cyclic alkanes using in-situ generation and on-site consumption of chlorine gas

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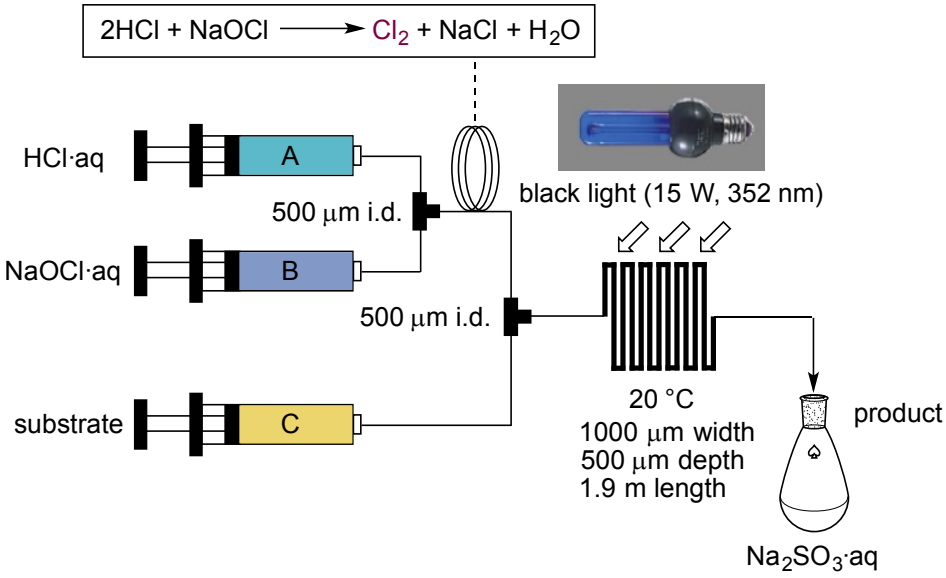
1. General information

Microflow chlorination was carried out by using a Mikroglas Dwell Device, (1000 μm width, 500 μm depth, and 1.9 m length, and total hold-up volume: 0.95 mL, Foturan® glass, Mikroglas Chemtech GmbH, Germany). Photo-irradiation was carried out by using a 15 W black light (Toshiba Lighting & Technology Co.). Two T-shaped micromixers, GL Science P-727 (PEEK, i.d. = 500 μm), were used for flow chlorination. GC analysis was performed with a SHIMADZU GC-2014 gas chromatography equipped with flame ionization detector using a fused capillary column; column (J&W DB-1 (ID: 0.32 mm, length: 30 m, Film: 1 μm), N_2 (700 kPa); temperature program: 60 °C for 6 min, then 60 °C to 250 °C at 20 °C/min. GC yields were determined by comparing the peak area with that of the standard solution containing an authentic sample. GC-MS analyses were performed with a shimadzu GCMS-QP2010 mass spectrometer. All products are known and commercially available; GC-MS spectrums of the products are in agreement with that of the authentic samples.

2. Microflow System for Flow Chlorination.



The microflow system for photo chlorination was comprised of two T-shaped micromixers (i.d. = 500 μm, PEEK), the Mikroglas photo-microreactor, and PTFE tubes.

Substrate, HCl·aq, and NaOCl·aq were introduced by means of syringe pumps. The photo-microreactor has two separate channels. One channel through which water flows is a heat exchanger, allowing to examine the photoirradiation reaction at a controlled temperature (20 °C). The PTFE tube between two mixers has 1 mm i.d. and 1 m length. The photo-microreactor was irradiated using a 15 W black light, 1 cm from the reactor. The reaction mixture eluted from the outlet was collected in a flask containing 10% Na_2SO_3.

3. Typical Procedure for Photo Chlorination by in-situ Generated Cl_2.

2 M HCl (2 mL, 4 mmol) and 1.9 M NaOCl (1 mL, 1.9 mmol) were placed in 5 mL gas-tight syringes and introduced by the syringe pumps to the first micromixer with 16.2 mL/h and 8.6 mL/h flow rates respectively. The mixture was then passed through the PTFE tube (1 mm i.d. x 1 m), which is connected to the second micromixier. Cyclohexane (**1a**, 3.5 mL, 32.4 mmol) was placed in a 10 mL gas-tight and introduced to the second micromixer with 32.3 mL/h flow rate. The resulting mixture was then passed through Mikroglas Dwel Device, which was cooled with water, under photo irradiation using a 15 W black light. The reaction mixture eluted from the outlet was collected in a flask containing 10% Na_2SO_3. The organic layer was easily separated from aquesou layer, and yield of chlorocyclohexane (**2a**) was determined by GC analysis (94% yield) by comparing the peak area with that of the standard solution containing an authentic chlorocyclohexane (**2a**).