Highly efficient and selective photoreaction progress under microflow conditions

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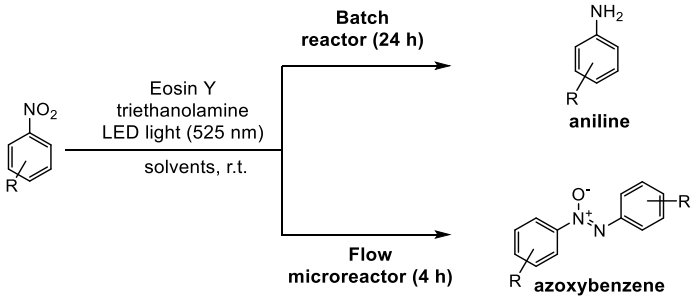
The hydrogenation (reduction) of nitrobenzenes is an important reaction to provide various important products (aniline, azobenzene, etc.) in industry. However, nitrobenzenes which have reducible groups show the poor product selectivity in this reaction due to the difference of the reductive property of each functional group containing nitro group. Recently, it was reported that simple photocatalytic reduction of nitrobenzenes to anilines in batch with green LED light irradiation (525 nm).[1] This reaction affords aniline derivatives dominantly irrespective of the existence of other functional groups; however, it needs very long photoirradiation time (24 h) to the full conversion.[1] Microreactors which have very narrow channels, have many advantages for proceeding organic reactions efficiently. Especially, because of the very short path length, organic photoreactions in flow microreactors can proceed very smoothly compared to those in batch reactor.[2] In this work, we performed the above photoreductions in a flow microreactor in order to improve the reaction efficiency.

Consequently, nitrobenzenes were smoothly converted for 4 h photoirradiation, but different product selectivity was observed (azoxybenzenes were obtained as main products instead of anilines). In addition, even in flow microreactor, the flow rate significantly affected the chemical yield of azoxybenzene. Especially, the high flow rate afford azoxybenzene in very high yield. These results showed that the condensation reaction of nitrosobenzenes and *N*-phenylhydroxylamines, which are the intermediates in the hydrogenation of nitrobenzenes, was proceeded very smoothly in the microreactor. This reactor-dependent results were successfully applied to some kinds of substrates.[3] In this symposium, we will show further microreactor-dependent reaction results for the synthesis of various kinds of azoxybenzenes.



1) B. Chen, et al. *Green Chem.* **2014**, *16*, 1082. 2) ex.) K. Mizuno, et al. *J. Photochem. Photobiol. C* **2016**, *29*, 107. 3) Y. Nishiyama, et al. *React. Chem. Eng.* **2019**, *4*, 2055.