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Highly-Efficient Photoreaction Using Microfluidic Device

Shigenori Togashi, Yukako Asano

***Abstract*—**We developed an effective microfluidic device for photoreactions with low reflectance and good heat conductance. The performance of this microfluidic device was tested by carrying out a photoreactive synthesis of benzopinacol and acetone from benzophenone and 2-propanol. The yield reached 36% with an irradiation time of 469.2 s and was improved by more than 30% when compared to the values obtained by the batch method. Therefore, the microfluidic device was found to be effective for improving the yields of photoreactions.

***Keywords*—**Microfluidic device, Photoreaction, Benzophenone, Black Aluminum Oxide, Detection, Yield Improvement.

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I. Introduction

PHOTOREACTIONS are caused by light (photon) and the reactants go through electronically excited states with high reaction activities, such as much higher energies, different molecular geometries, and different molecular configuration. Compounds are known to exhibit different chemical behaviors in their excited states when compared to those in their ground state [1]. Therefore, photoreactions allow for the simplification of complicated chemical syntheses, and have been considered as environmentally benign reactions. Various kinds of photoreactions are known to occur under the influence of visible or ultraviolet light. However, photoreactions proceed less effectively by used of batch reactors because it is difficult to homogeneously irradiate light throughout the reactors from the top of the bottom.

Recently, microfluidic devices with micro channels on the scales of micrometers have attracted much attention owing to their ability to permit the occurrence of chemical reactions in a reaction space that is several orders of magnitude smaller than that in conventional batch reactors [2], [3]. In microfluidic devices, the effects of parameters associated with surface, diffusion, heat transfer, viscosity, and surface tension are pronounced, while the effects of parameters associated with volume, mass, and inertia force are small. In a small reaction space that exhibits a high surface-to-volume ratio, microfluidic devices enable fast mixing and allow for accurate thermal and reaction time control [4], [5]. Because of these features, microfluidic devices enable better control of chemical reactions, acceleration of reaction rates and improved yields. This has been reported for various reactions including Friedel-Crafts monoalkylation [6], Grignard-based reactions [7], and Sonogashira coupling [8].

It is known that a variety of photoreactions proceed more effectively through micro channels in microfluidic devices, rather than in batch reactors, which typically exhibit low efficiencies [9], [10]. This has been reported less extensively, although the differences in the efficiencies of some reactions including pinacol formation reaction [11], cyanation [12], photocatalysis employing titanium dioxide photocatalyst [13], and photocyclo addition [14]-[17] have been observed. Some photoreactions, in particular, have been performed using energy-saving low-power black light and ultraviolet LED (light emitting diode) sources.

However, current microfluidic devices used for photoreactions that are made of quartz glass may cause inaccurate temperature control and vaporization of liquid components because of the low heat conductance. They may also cause instability in terms of the incident light wavelength originating from the heating of the light source, owing to diffuse reflection to the bottom surface of channels. The diffuse reflection depends on the accuracy of processing of the bottom surface of the channels.

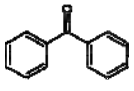
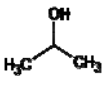
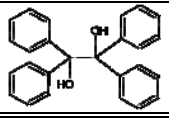
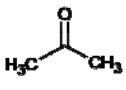
In this study, we developed effective microfluidic devices for photoreactions that used a black aluminum oxide channel substrate with low reflectance and good heat conductance, which can be applied in photoreactions. The performance of this microfluidic device was tested by carrying out a photoreactive synthesis of benzopinacol and acetone from benzophenone and 2-propanol.

II. Photoreactive Synthesis of Benzopinacol

The target reaction is the photoreactive synthesis of benzopinacol and acetone from benzophenone and 2-propanol as shown in chemical reaction (1) and Table I. This reaction is known to need long reaction times (i.e., more than 24 h) by the batch method [18].

$$\text{Benzophenone} + 2-\text{Propanol} \xrightarrow{h\gamma=366nm} \text{Benzopinacol} + \text{Acetone} \quad (1)$$

TABLE I
Details of Photoreactive Synthesis

Benzophenone	2-Propanol	Benzopinacol	Acetone
			

III. Microfluidic Device for Photoreaction

Fig. 1 shows the configuration of a microfluidic device. The microfluidic device consisted of a channel plate obtained by

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Open Science Index, Chemical and Molecular Engineering Vol:8, No:8, 2014 publications.waset.org/9998903/pdf

welding two substrates and three holder parts made of stainless steel. The holders that exhibited good heat conductance might contribute to the removal of heat from the microfluidic device plate.

Fig. 2 shows photograph of the assembled microfluidic device. The channel width was set to 1.0 mm. The channel depth was set to 0.2 mm and 1.0 mm in order to represent the features of a "micro" scale device as shown in Table II. The channel plate constructed with quartz glass as the top substrate and black aluminum oxide as the channel substrate might have furnished.

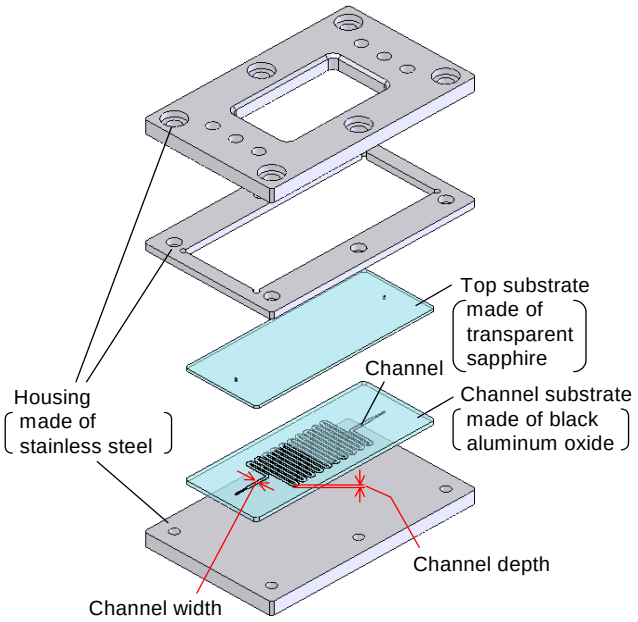


Fig. 1 Configuration of a microfluidic device

TABLE II
SPECIFICATIONS OF MICROFLUIDIC DEVICES

	Micro-1	Micro-2
Channel width [mm]	1.0	1.0
Channel depth [mm]	0.2	1.0

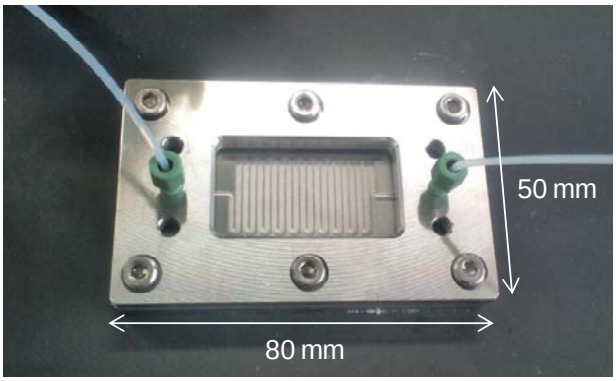


Fig. 2 Photograph of the assembled microfluidic device

IV. EXPERIMENTAL METHOD

The reaction solution with the concentration of 0.5 mol/L (0.5 kmol/m^3) was obtained by dissolving benzophenone in 2-propanol [19]. No catalyst such as glacial acetic acid was added to this solution.

Fig. 3 shows the schematic of the microfluidic device system used in this study. The reaction solution of benzophenone in 2-propanol was introduced into the microfluidic device through the polytetrafluoroethylene (PTFE) tube. The microfluidic device was exposed to an ultraviolet LED source (wavelength $h\nu$ = 365 nm) to carry out the reaction. The product solution was obtained from the microfluidic device through the PTFE tube and collected in a vessel filled with acetone. The outlet of the tube was immersed into acetone to prevent the precipitation of benzophenone and benzopinacol bearing in mind that 2-propanol and acetone vaporized readily. The time period of irradiation was controlled from 46.9 to 469.2 s within the controllable flow rates, and the reaction temperature was set at room temperature (296–297 K).

The batch syntheses were also performed for comparison. The reaction solution (10 mL, 1.0×10^{-5} m^3) was stirred in a 20 mL (2.0×10^{-5} m^3) vessel with a depth of about 10 mm being irradiated by the LED source. The reaction temperature was set at room temperature (296–297 K).

The benzophenone and benzopinacol in the product solution were analyzed by high performance liquid chromatography (HPLC) produced by Hitachi High Technologies, Ltd. using the analysis conditions. The photoreaction yield of benzophenone was obtained as defined by (2).

$$\text{Yield}[\%] = \frac{[\text{Benzopinacol}]}{\frac{\text{B[enzophenone]}}{2}+[\text{Benzopinacol}]} \times 100 \qquad (2)$$

Here, [C] indicates the concentration of the substance C. Note that one mole of benzopinacol is obtained from two equivalents of benzophenone.

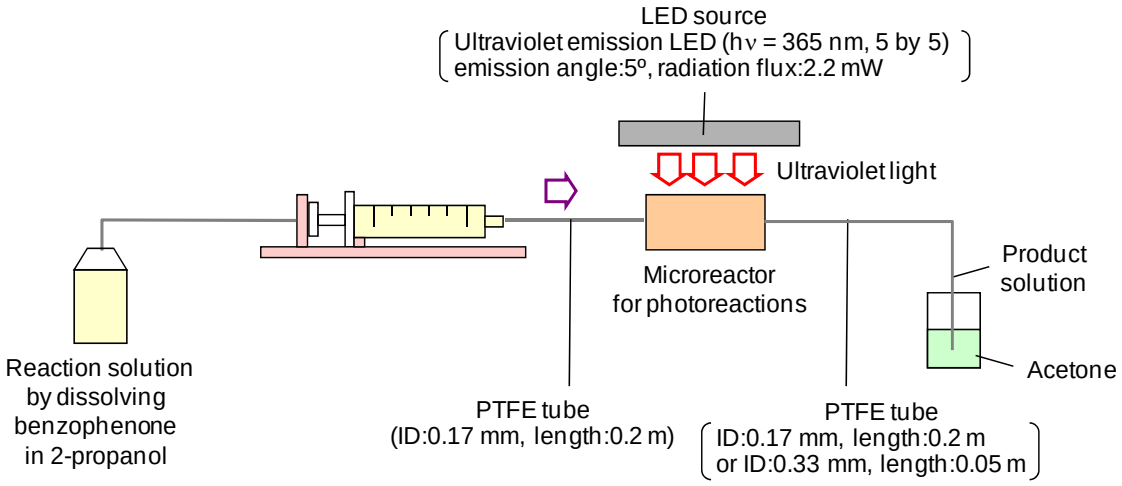


Fig. 3 Schematic of the microfluidic device system used in this study

It is known that the light intensity of a LED is unstable even just after it begins irradiating light. The LED becomes heated and the wavelength of light becomes unstable, as the irradiation is prolonged over a period of time. Furthermore, it is estimated that the intensity of light becomes inhomogeneous because the emission angle leads to overlapping intensities.

Therefore, we measured the dependence of the light intensity on the irradiation time when the working distance (WD) between the LED source and the measurement position was set to 20 mm or 60 mm as shown in Fig. 4. We used the ultraviolet emitting LEDs (wavelength: 365 nm, emission angle: 5º, and radiation flux: 2.2 mW) from Nichia Corporation. The LED source consisted of a 5 × 5 matrix of 25 LEDs at an interval of 8 mm. The measurement position was defined as an extension of the center or edge of the LED source.

Fig. 5 shows the light intensity of the LED source used in this study. More than 7 min was needed until the light intensity was stable at an extension of the center of the LED source, while a few minutes were required to achieve stable intensity when the extension was measured at an extension of the edge of the LED source. At a WD of 20 mm, the difference in the light intensity by the measurement positions was only about 0.3 mW/cm^2 (3 × 10^3 mW/m^2), while at a WD of 60 mm, the difference was about 0.8 mW/cm^2 (8 × 10^3 mW/m^2). The light intensity depended largely on the measurement positions. The overlap between the radiation was small at shorter *WD* because the emission angle was only 5º. However, the overlap became larger at larger WD and the influence caused by the overlap became larger particularly at an extension of the edge of the LED source.

The difference in the light intensity was considered to be small in the channels of the microfluidic device for photoreactions, when the difference in the measured intensity between at extensions of the center and edge was small. Therefore, we set the WD at the shortest possible value of 20 mm and began the experiments after the LED source had irradiated light for more than 10 min.

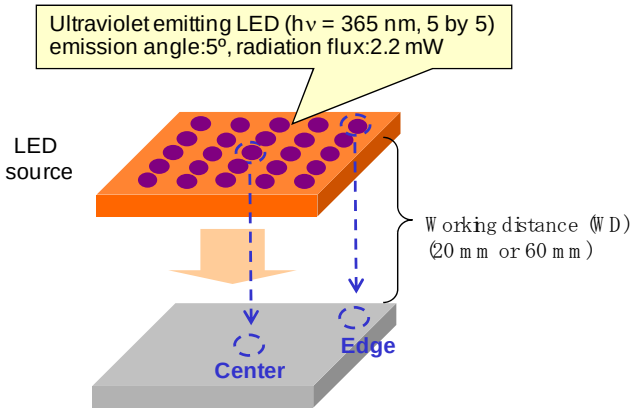


Fig. 4 Diagram showing the system used for measuring the light intensity of the LED source used in this study

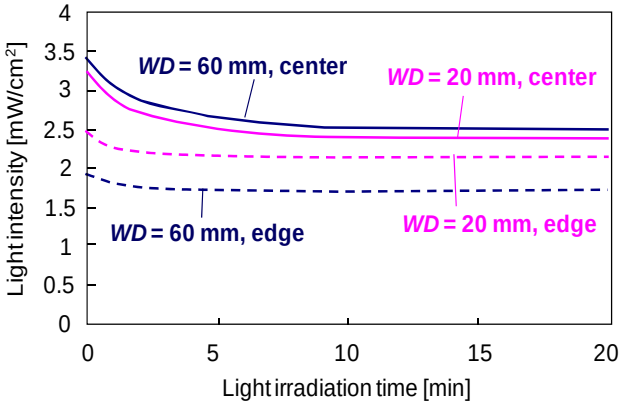


Fig. 5 Light intensity of the LED source used in this study

V. Experimental Results

We measured the yield of the photoreaction of benzophenone by changing the irradiation time from 46.9 to 469.2 s and studied the differences in the efficiencies exhibited by the two kinds of microfluidic devices.

Fig. 6 shows the yields of the photoreaction of

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benzophenone. The upper horizontal axis shows the flow rates corresponding to the irradiation time shown in the lower horizontal axis. The reaction proceeded more rapidly in Micro-1 with shallower channels than in Micro-2. Under the conditions of high concentration of benzophenone (0.5 mol/L (0.5 kmol/m^3)) used in this study, most of the incident light was absorbed when the channel depth was ~0.25 mm. In the channels with a channel depth of 1 mm, therefore, about one-fourth of the solution (measured from the top) contributed to the photoreaction. In reactor 1, the channels remained unblocked at an irradiation time for more than 187.7 s, which corresponded to flow rates of less than 0.025 mL/min (2.5×10^{-8} m^3/min). The yield reached 36% with an irradiation time of 469.2 s and was improved by more than 30% in comparison to values achieved by the batch method. This was because heat converted from the incident light was quickly removed at the bottom surface of the channels with better heat conductance and the liquid components hardly vaporized. Therefore, it was confirmed that the microfluidic device method with shallow channels was effective for achieving high yields in photoreactions.

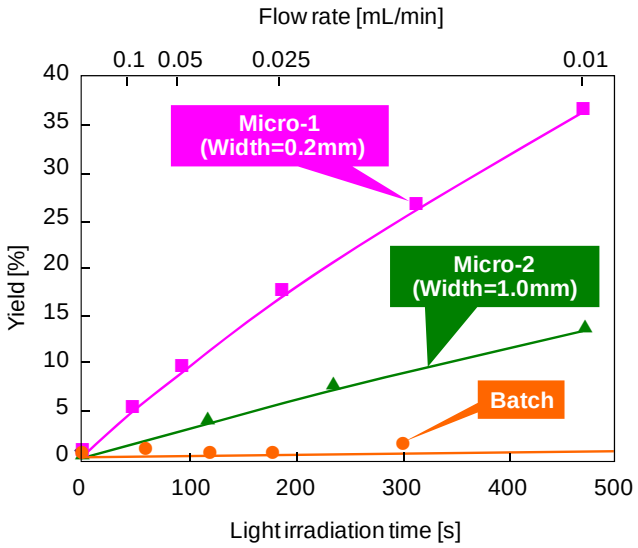


Fig. 6 Yields of the photoreaction of benzophenone

REFERENCES

[1] Roberts, J. D. and M. C. Caserio; Basic Principles of Organic Chemistry, 2nd ed., W. A. Benjamin, Inc., Menlo Park, CA, USA, 1977.
[2] Hessel, V., S. Hardt and H. Löwe eds.; Chemical Micro Process Engineering: Fundamentals, Modeling and Reactions, Wiley-VCH, Weinheim, Germany, 2004.
[3] Hessel, V., H. Löwe, A. Müller and G. Kolb eds.; Chemical Micro Process Engineering: Processing and Plants, Wiley-VCH, Weinheim, Germany, 2005.
[4] Benson, R. S. and J. W. Ponton; "Process Miniaturisation—A Route to Total Environmental Acceptability?," *Chem.Eng.Res.Des.*, A71, 1993, pp.160-168.
[5] Schubert, K., W. Bier, W. Keller, G. Linder and D. Seidel; "Gas to Gas Heat Transfer in Micro Heat Exchangers," *Chem. Eng. Process.*, 32, 1993, pp.33-43.
[6] Suga, S., A. Nagaki and J. Yoshida; "Highly Selective Friedel–Crafts Monoalkylation Using Micromixing," *Chem. Commun.*, 3, 2003, pp.354-355.
[7] Taghavi-Moghadam, S., A. Kleemann and K. G. Golbig; "Microreaction Technology as a Novel Approach to Drug Design, Process Development and Reliability," *Org. Process. Res. Dev.*, 5, 2001, pp.652-658.
[8] Fukuyama, T., M. Shinmen, S. Nishitani, M. Sato and I. Ryu; "A Copper-Free Sonogashira Coupling Reaction in Ionic Liquids and its Application to a Microflow System for Efficient Catalyst Recycling," *Org. Lett.*, 4, 2002, pp.1691-1694.
[9] Yoshida, J. ed.; Microreactors, Epoch-making Technology for Synthesis (Maikuroriakuta, Shinjidai no Gouseigijutsu), CMC Publishing Co., Ltd., Tokyo, Japan, 2003.
[10] Matsushita, Y., T. Ichimura, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, H. Tanibata and T. Murata; "Recent Progress on Photoreactions in Microreactors," *Pure Appl. Chem.*, 79, 2007, pp.1959-1968.
[11] Lu, H., M. A. Schmidt and K. F. Jensen; "Photochemical Reactions and On-Line UV Detection in Microfabricated Reactors," *Lab Chip*, 1, 2001, pp.22-28.
[12] Ueno, K., F. Kitagawa and N. Kitamura; "Photocyanation of Pyrene across and Oil/Water Interface in a Polymer Microchannel Chip," *Lab Chip*, 2, 2002, pp.231-234.
[13] Gorges, R., S. Meyer and G. Kerisel; "Photocatalysis in Microreactors," *J. Photochem. Photobiol. A*, 167, 2004, pp.95-99.
[14] Fukuyama, T., Y. Hino, N. Kamata and I. Ryu; "Quick Execution of [2+2] Type Photochemical Cycloaddition Reaction by Continuous Flow System Using a Glass-made Microreactor," *Chem. Lett.*, 33, 2004, pp.1430-1431.
[15] Fukuyama, T., Y. Kajihara, Y. Hino and I. Ryu; "Continuous Microflow [2+2] Photocycloaddition Reactions Using Energy-Saving Compact Light Sources," *J. Flow Chem.*, 1, 2011, pp.40-45.
[16] Maeda, H., H. Mukae and K. Mizuno; "Enhanced Efficiency and Regioselectivity of Intramolecular [2+2] Photocycloaddition of 1-Cyanonaphthalene Derivative Using Microreactors," *Chem. Lett.*, 34, 2005, pp.66-67.
[17] Sugimoto, A., T. Fukuyama, Y. Sumino, M. Takagi and I. Ryu;"Microflow Photo-Radical Reaction Using a Compact Light Source: Application to the Barton Reaction Leading to a Key Intermediate for Myriceric Acid A," *Tetrahedron*, 65, 2009, pp.1593-1598.
[18] Pitts, J. N., Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Reckten wald and R. B. Martin; "Photochemical Reactions ofBenzophenone in Alcohols," *J. Am. Chem. Soc.*, 81, 1958, pp.1068-1077.
[19] Lu, H., M. A. Schmidt and K. F. Jensen; "Photochemical Reactions and On-Line UV Detection in Microfabricated Reactors," *Lab Chip*, 1, 2001, pp.22-28.

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