## Efficient Synthetic Photocyclization for Phenacenes Using a Continuous Flow Reactor

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The continuous flow reaction technique has been applied to the photocyclization of 1,2-diarylethenes, the so-called Mallory reaction, to afford phenacenes in high chemical yields and efficiencies ( $114-288 \text{ mg h}^{-1}$ ). The present technique will allow us to produce several grams of phenacenes at a time.

Aromatic molecules with an extended  $\pi$  system have attracted considerable interest because of their importance from the aspects of organic electronic materials such as organic semiconductors.<sup>1</sup> In the past two decades, acenes, represented by pentacene, have been extensively studied as a potential active layer in organic field-effect transistors (OFETs).<sup>2</sup> Acenes with extended  $\pi$  conjugation are, however, generally unstable on exposure to oxygen and light.<sup>3,4</sup> Thus, it is necessary to develop a post-pentacene organic material possessing high chemical stability and excellent OFET performance.

We have demonstrated that picene ([5]phenacene) shows very high p-channel OFET performance. The field-effect carrier mobility  $\mu$  of picene was ca.  $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1.5}$  Additionally, picene displays superconductivity upon doping with alkali metals such as potassium.<sup>6</sup> Recently, we have found that fulminene ([6]phenacene) is a suitable material for the active layer of p-channel OFETs ( $\mu = 7.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).<sup>7</sup> [7]Phenacene also serves as the active layer of OFETs ( $\mu = 0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).<sup>8</sup> As phenacenes are quite stable on exposure to air and light, they are promising organic electronic materials.9 Moreover, concerning the fundamental photophysical behavior, picene displays fluorescence emission from the second lowest excited singlet  $(S_2)$  state in the vapor phase.<sup>10</sup> Thus, the photophysical features of phenacenes are also of interest. In order to promote more extensive and intensive investigations on the solid-state electronics and photophysical features of phenacenes, a simple and efficient synthetic process for supplying them on a practical scale is highly desired.<sup>11</sup>

Conventionally, phenacene skeletons have been constructed via the photocyclization of 1,2-diarylethene (the Mallory photocyclization, Scheme 1).<sup>12</sup> Although the Mallory photoreaction is an excellent procedure for phenacene synthesis, it is necessary to increase the efficiency. In the present study, we have applied a



**Scheme 1.** General reaction scheme of the Mallory photocyclization.

continuous flow reaction technique to the Mallory photoreaction. Flow photoreaction technique has merits to overcome the drawbacks due to conventional batch photolysis, i.e., shortening irradiation time, suppressing the secondary photoprocesses, no limitations in the reaction scale, etc.<sup>13</sup> Since very few literature reports are available for the Mallory photocyclization using a flow technique,<sup>14</sup> we have fabricated a flow photolysis system according to the paper by Booker-Milburn.<sup>15</sup> With the established system, various phenacenes have been efficiently prepared. Herein, we report the results of the flow photolysis.

The flow photoreactor was fabricated according to the literature.<sup>15</sup> It consists of a tetrafluoroethylene–hexafluoropropylene copolymer (FEP) tube (2 mm × 10 m), a 450-W high-pressure Hg arc lamp (Pyrex-filtered,  $\lambda > 280$  nm), and a ceramic plunger pump (Figure S1, Supporting Information).<sup>16</sup> The 1,2-diarylethene substrates used in this study were prepared by the Wittig reaction between the corresponding arylaldehydes and (arylmethyl)triphenylphosphonium salts. The *E–Z* mixtures thus obtained were used for the photocyclization without separation because the *E*-diarylethene, which was unfavorable for the photocyclization, isomerized to the favorable *Z*-isomer under the photolysis conditions.<sup>12</sup>

We investigated the photocyclization of 2-methylstilbene (2MS) to 1-methylphenanthrene (1MP) as a pilot reaction to examine the flow-photolysis conditions because the latter is an important platform for the synthesis of higher phenacenes.<sup>17,18</sup> Figure 1 compares the photolysis results obtained by conventional batch irradiation with those by the flow reaction.

As seen in Figure 1a, upon the batch photolysis of 2MS (5 mM in cyclohexane) in the presence of  $I_2$  (0.1 equiv), 2MS was consumed almost completely after 8 h of irradiation and 1MP was formed in up to 80% yield.

Figure 1b summarizes the flow reaction results, showing the 2MS consumption and 1MP yields for different residence times. The residence time implies the period during which the reactant solution flows through the flow-reactor tube. Thus, it is equivalent to the irradiation time. Six minutes of irradiation resulted in complete 2MS consumption and quantitative 1MP formation. By using the developed flow system, the irradiation time was drastically shortened, and the 1MP yield was significantly improved as compared to those in batch photolysis.

For a preparative scale flow reaction, 2.00 g of 2MS was converted to 1MP (1.83 g, 92%) in 6.7 h. By contrast, for a batch photolysis of 0.56 g of 2MS with 28 h irradiation, 0.44 g (76%) of 1MP was obtained after chromatographic separation. These results clearly show the advantages of the flow reaction technique over the conventional batch photolysis.

Entry	Substrate		Product		Solvent	Residence time <sup>b</sup>	Isolated yield
Enuy						(Flow rate)	(Production efficiency) <sup>c</sup>
1		(40 mg)		(18 mg)	Cyclohexane	6 min	98%
1		(49 mg)		(48 mg)	(50 mL)	$(5 \mathrm{mLmin^{-1}})$	$(288 \mathrm{mg}\mathrm{h}^{-1})$
2 <sup>d</sup>	$\bigtriangledown \bigcirc \bigcirc$	(19 mg)		(13 mg)	Cyclohexane	13 min	70%
					(10 mL)	$(50\mu Lmin^{-1})$	$(4 \mathrm{mg}\mathrm{h}^{-1})$
3	$\bigcirc - \frown \bigcirc$	(45 mg)	$\bigcirc \bigcirc \bigcirc$	(43 mg)	Cyclohexane	8 min	96%
					(50 mL)	$(3.4 \mathrm{mLmin^{-1}})$	$(175 \mathrm{mg}\mathrm{h}^{-1})$
4		(100 mg)		(91 mg)	Cyclohexane	6 min	91%
					(100 mL)	$(5 \mathrm{mL}\mathrm{min}^{-1})$	$(273 \mathrm{mg}\mathrm{h}^{-1})$
5		(50 mg)		(45 mg)	Cyclohexane	6 min	92%
					(50 mL)	$(5 \mathrm{mL}\mathrm{min}^{-1})$	$(270 \mathrm{mg}\mathrm{h}^{-1})$
6		(70 mg)		(54 mg)	Cyclohexane	8 min	78%
					(50 mL)	$(3.4 \mathrm{mLmin^{-1}})$	$(220 \mathrm{mg}\mathrm{h}^{-1})$
7		(52 mg)		(38 mg)	Toluene	6 min	73%
					(100 mL)	$(5 \mathrm{mLmin^{-1}})$	$(114 \mathrm{mg}\mathrm{h}^{-1})$
8		(35 mg)		(28 mg)	Toluene	10 min	80%
0		(55 mg)		(20 mg)	(200 mL)	$(3 \mathrm{mLmin^{-1}})$	$(168 \mathrm{mg}\mathrm{h}^{-1})$
9	$\sum \sum$	(100 mg)		(89 mg)	Cyclohexane	6 min	89%
					(100 mL)	$(5 \mathrm{mLmin^{-1}})$	$(267 \mathrm{mg}\mathrm{h}^{-1})$
10	668	(100 mg)		(54 mg)	Toluene	8 min	53%
					(50 mL)	$(3.4 \mathrm{mLmin^{-1}})$	$(220 \mathrm{mg}\mathrm{h}^{-1})$
11		(100 mg)		(74 mg)	Toluene	6 min	74%
					(100 mL)	$(5 \mathrm{mLmin^{-1}})$	$(222 \mathrm{mg}\mathrm{h}^{-1})$

<sup>a</sup>Under aerated conditions, in the presence of I<sub>2</sub>. <sup>1</sup>H NMR spectra of the obtained phenacenes are shown in Figure S2, Supporting Information.<sup>16</sup> <sup>b</sup>Residence time = (inside volume of the reactor)/(flow rate). <sup>c</sup>Production efficiency = (obtained product amount)/ [(solvent volume)/(flow rate)]. <sup>d</sup>Photoreaction was performed by using a commercial microreactor.<sup>19</sup>



**Figure 1.** (a) Time profiles for photocyclization of 2MS to 1MP for batch irradiation. (b) The residence-time dependence of 2MP consumption and 1MP formation: In aerated cyclohexane (5 mM) in the presence of  $I_2$  (0.1 equiv).

The flow reaction technique has been applied to synthesize other phenacenes. The results are summarized in Table 1. Since the product yield and total reaction time for the flow photolysis depend on the volume of the reactant solutions flowed through the reactor, the photolysis efficiency is evaluated by the production efficiency (amount of the product obtained in unit time, mg h<sup>-1</sup>) as well as the isolated chemical yield (%). Using the optimized irradiation conditions for 2MS (6 min of irradiation time, cf. Figure 1b), 1MP was obtained in 98% chemical

yield and  $288 \text{ mg h}^{-1}$  of the production efficiency (Entry 1). By an examination using a commercially available microflow reactor,<sup>19</sup> 2MS was obtained only in 70% yield with a production efficiency of  $4 \text{ mg h}^{-1}$  (Entry 2). Consequently, the chemical vield for the present flow-reactor photolysis was higher than that for the microreactor photolysis. Phenanthrene, chrysene, and picene were obtained in excellent chemical yields >90% (Entries 3-5). Photocyclization of 1.0 g of 1,2-di(1naphthyl)ethene produced 0.93 g (95%) of picene. This result indicates that a gram-scale photoreaction is possible with the present flow reactor. Photocyclization of 1-styrylphenanthrene was also suitable for picene preparation (78%, Entry 6), although the yield was slightly lower than that for the photoreaction of dinaphthylethene (Entry 5). Fulminene and [7]phenacene were also prepared in good chemical yields, 73% and 80%, respectively (Entries 7 and 8), which were higher than the reported yields for conventional batch photolysis.<sup>17,18</sup> Methyl-substituted phenacenes, which are potential precursors to higher phenacenes,<sup>17,18</sup> were prepared in moderate to high chemical yields and production efficiencies (Entries 9-11).

In summary, a preparative-scale continuous flow reaction technique was applied to the Mallory photocyclization. Various phenacenes were prepared in high chemical yields and production efficiencies. With the present flow system, several grams of phenacenes can be readily obtained in one day. Since phenacenes are gaining more importance as organic-electronic materials, their fundamental and application studies will be promoted by the efficient supply of phenacene in large quantities. The present work was supported by a Grant-in-Aid for Scientific Research, KAKENHI (Nos. 23350059 and 24550054) from JSPS and partly performed under the Cooperative Research Program of the "Network Joint Research Center for Materials and Devices."

## **References and Notes**

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