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Diarylethenes by Introduction
of Substituents at the Reactive
Carbons

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Control of Cycloreversion Quantum Yields of Diarylethenes by Introduction of Substituents at the Reactive Carbons

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Several diarylethene derivatives having various substituents at the reactive carbons were prepared and the quantum yields were measured. Although the cyclization quantum yields were scarcely affected by the introduction of substituents, the cycloreversion quantum yields varied depending on the substituents.

Keywords: diarylethene; photochromism; quantum yield; substituent effect

INTRODUCTION

Photochromic compounds undergo reversible isomerization between two isomers having different absorption spectra upon irradiation with appropriate wavelength of light [1]. Among these photochromic compounds, diarylethenes have attracted much attention because they undergo thermally irreversible and fatigue-resistant photochromic reactions. Various diarylethene derivatives have been synthesized so far in an attempt to apply them to optoelectronic devices such as memories and switches [2].

Control of quantum yields is one of the most fundamental issues of molecular design. In order to control the cycloreversion quantum yields of diarylethenes we took a novel strategy to introduce various

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1a: R = OCH3
 1b: R = OCH3

 2a: R = CN
 2b: R = CN

 3a: R =
$$---$$
Ph
 4b: R = $--$ CH2CH2CH3

 5a: R = CH=C(CH3)2
 5b: R = CH=C(CH3)2

 6a: R = CH2OCH3
 6b: R = CH2OCH3

 7a: R = CH3
 7b: R = CH3

 8a: R = OCH3
 9b: R = CN

 10a: R = $--$ Ph
 10b: R = $--$ Ph

 11b: R = $--$ CH2CH2CH3
 11b: R = $--$ CH2CH2CH3

 12a: R = CH3
 12b: R = CH3

SCHEME 1 Chemical structure and photochromism of diarylethene derivatives.

substituents at the reactive carbons [3]. Herein we report on photochromic properties of several diarylethene derivatives having various substituents at the reactive carbons as shown in Scheme 1.

RESULTS AND DISCUSSION

Photochromic Reaction

The synthesis of diarylethene derivatives was carried out according to the general synthetic procedure [4]. Each diarylethene underwent photochromism upon irradiation with appropriate wavelength of light in hexane. Colorless solutions of the diarylethene derivatives turned blue, purple, red, and orange, depending on the substituents at the

•		
$\lambda_{ ext{max}}/ ext{nm}^a$	$\Phi_{\mathbf{a} ightarrow \mathbf{b}}{}^{b}$	$\Phi_{\mathrm{b} o\mathrm{a}}{}^c$
625	0.44	1.7×10^{-5}
545	0.42	0.41
575	0.17	0.32
575	0.41	0.27
625	0.25	0.23
580	0.50	0.0062
575	0.59	0.013
547	0.34	0.030
496	0.28	0.59
520	0.13	0.55
520	0.21	0.58
517	0.35	0.35
	625 545 575 575 625 580 575 547 496 520 520	625 0.44 545 0.42 575 0.17 575 0.41 625 0.25 580 0.50 575 0.59 547 0.34 496 0.28 520 0.13 520 0.21

TABLE 1 Absorption Maxima of Closed-ring Isomers and Quantum Yields in Hexane

reactive carbons. The absorption maxima of close-ring isomers are summarized in Table 1.

Quantum Yield

The cyclization and cycloreversion quantum yields in hexane at room temperature are shown in Table 1. The cyclization quantum yields are close to the values of methyl derivatives **7a** and **12a**, and scarcely affected by modification of substituents at the reactive carbons. Conversely, the cycloreversion quantum yields varied depending on the substituents. Methoxy groups extremely suppressed the cycloreversion reactivity to less than 10^{-4} . However, cyano and π -conjugated groups enhanced the reactivity. The substituent effect was independent of the aryl groups, and similar tendency was observed for benzothiophene derivatives. The cycloreversion quantum yields of **2b** and **9b** were obtained to be 0.41 and 0.59 which are 30 and 1.7 times larger than those of **7b** and **12b**, respectively. We can control the cycloreversion reactivity of the diarylethenes as much as 24000 times.

REFERENCES

- [1] (a) Brown, G. H. (1971). *Photochromism*, Wiley-Interscience: New York.
 - (b) Dürr, H. & Bouas-Laurent, H. (1990). *Photochromism: Molecules and Systems*, Elsevier: Amsterdam.
- [2] (a) Irie, M. (2000). Chem. Rev., 100, 1685.

^aAbsorption maxima of the closed-ring isomers in the visible region.

^bCyclization quantum yield.

^cCycloreversion quantum yield.

- (b) Irie, M. & Uchida, K. (1998). Bull. Chem. Soc. Jpn., 71, 985.
- [3] (a) Shibata, K., Kobatake, S., & Irie, M. (2001). Chem. Lett., 618.
 - (b) Morimitsu, K., Shibata, K., Kobatake, S., & Irie, M. (2002). J. Org. Chem., 67, 4574.
 - (c) Morimitsu, K., Shibata, K., Kobatake, S., & Irie, M. (2002). Chem. Lett., 572.
 - (d) Morimitsu, K., Kobatake, S., Nakamura, S., & Irie, M. (2003). Chem. Lett., 32, 858
 - (e) Morimitsu, K., Kobatake, S., & Irie, M. (2004). Tetrahedron Lett., 45, 1155.
- [4] (a) Irie, M., Lifka, T., Kobatake, S., & Kato, N. (2000). J. Am. Chem. Soc., 122, 4871.
 - (b) Irie, M., Sakemura, K., Okinaka, M., & Uchida, K. (1995). J. Org. Chem., 60, 8305.