

# Photo-Ring-Opening Efficiency of 2,2-Diphenyl-2*H*-1-benzopyran Evaluated from Addition Reactivity of Amines to Its Ring-Opened Isomers

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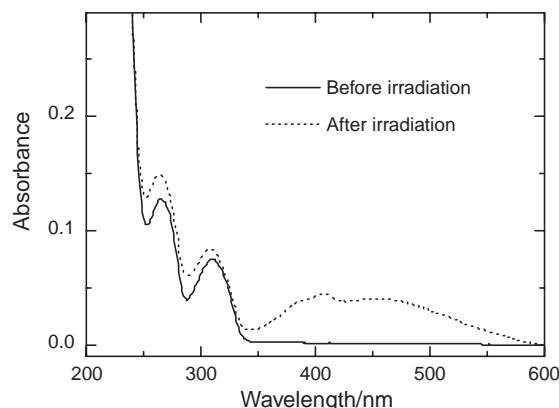
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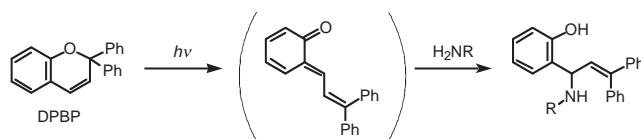
Irradiation of 2,2-diphenyl-2*H*-1-benzopyran (DPBP) in the presence of a primary or a secondary amine gave an addition product. With a large excess of amine, the apparent quantum yield for product formation reached 0.5. This value corresponds to a minimal quantum yield for formation of DPBP colored ring-opened forms.

2*H*-1-Benzopyran is a core unit of well-known photochromic compounds such as spirobifluorene.<sup>1</sup> On irradiation of 2,2-diphenyl-2*H*-1-benzopyran (DPBP), as an example, with UV light in solution, the colorless solution becomes pink. The structure of this colored photoproduct was proved to be a cyclohexadienone with a butadiene unit produced by opening of the pyran ring.<sup>2</sup> We reported dynamic behavior of the primary products of 2*H*-1-benzopyrans in the picosecond to millisecond time domain.<sup>3</sup> Methyl- or phenyl-substituted 2*H*-1-benzopyrans were reported to suffer methanol addition under illumination, and the adduct formation was attributed to a thermal process of the ring-opened forms of 2*H*-1-benzopyrans.<sup>4</sup> Recently, photoaffinity labeling of cytochrome P450 3A4 by lapachol, a naturally occurring 2*H*-naphthopyran, was reported.<sup>5</sup> This is a trapping of cysteine residues (RSH) by the primary photoproduct of the 2*H*-naphthopyran. We have investigated photochemical behavior of DPBP in the presence of amines, and have found that primary and secondary amines add effectively to the ring-opened form of DPBP. This reaction was applied to photo-initiated surface grafting methods on polymer film.<sup>6</sup> In the present work, the rates and efficiencies were measured for the addition of various amines to the ring-opened form of DPBP, and the quantum yield was estimated for the ring opening of DPBP.

On irradiation of a cyclohexane solution of DPBP at 313 nm, the color of the solution varied from initially colorless to pink; main absorption bands appeared around 410 and 455 nm (Figure 1). In the presence of butylamine, otherwise



**Figure 1.** Absorption spectra observed before and after irradiation of a cyclohexane solution of DPBP at 313 nm.



**Scheme 1.**

under the same conditions, the color was not changed at all upon irradiation, however. Evaporation of the amine and solvent from the reaction mixture gave a colorless oily product, which was proved to be a 1,4-adduct of the DPBP ring-opened form, 1,1-diphenyl-3-(2-hydroxyphenyl)-3-butylamino-1-propene by precise-mass (*m/e* 357.2123, C<sub>25</sub>H<sub>27</sub>NO) and proton NMR measurements (Scheme 1). The NMR spectrum displayed signals due to butyl-group protons, a methyne ( $\delta$  4.45, d), and an ethylenic proton ( $\delta$  6.30, d) instead of the ethylenic protons of the pyran ring ( $\delta$  6.20 and 6.58, d) of the starting DPBP. The signals due to the methyne and ethylenic protons are quite similar to those of the 1,4-adduct of DPBP and methanol reported by Padwa et al.<sup>4</sup> Propylamine, diethylamine, morpholine, piperidine, and 2-ethanolamine were also found to add to DPBP upon irradiation in cyclohexane and 1,4-dioxane under similar conditions. The adducts were formed almost quantitatively. Their molecular structures were proved to be similar to that of the butylamine adduct by comparing their NMR spectra. The 1,4-addition of amines was confirmed to be a thermal process by allowing an amine to react with DPBP after UV-irradiation. Actually, an acetonitrile solution of DPBP was irradiated at 313 nm for 30 s and morpholine was put into the reaction pot immediately after irradiation. The formation of the morpholine adduct was established by HPLC analysis.

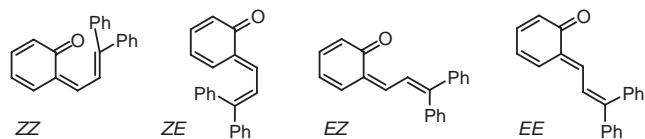
In order to ascertain this mechanism and to clarify the reaction process, decay behavior of the ring-opened form was investigated in the absence and presence of various amines and methanol. After irradiation of DPBP in solution for 60 s at 313 nm, disappearance of the ring-opened form was followed by measuring its absorbance at 410 nm at 20 °C. From the absorbance change, the first-order decay rate constants of the DPBP ring-opened form were determined, as listed in Table 1. The decay rate constants are smaller in heteroatom-containing solvents rather than in hydrocarbon solvents.

**Table 1.** Rate Constants for Decay of the DPBP Ring-Opened Form at 20 °C

Solvent	Rate constant/s <sup>-1</sup>	Lifetime/h
Cyclohexane	$8.9 \times 10^{-4}$	0.31
Hexane	$3.5 \times 10^{-4}$	0.79
Ethyl acetate	$1.2 \times 10^{-4}$	2.3
1,4-Dioxane	$3.8 \times 10^{-5}$	7.3
Acetonitrile	$2.8 \times 10^{-5}$	9.9
Tetrahydrofuran	$2.6 \times 10^{-5}$	11

**Table 2.** Rate Constants for Addition of Amines and Methanol to the DPBP Ring-Opened Form at 20 °C

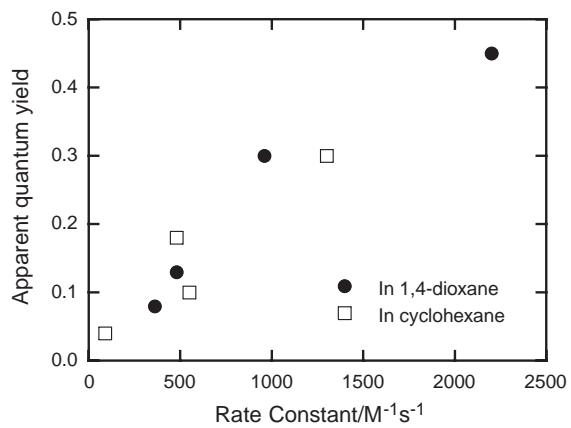
Addend	Rate constant/M <sup>-1</sup> s <sup>-1</sup>		pK <sub>b</sub>
	In 1,4-dioxane	In cyclohexane	
Piperidine	2200	1300	2.88
Morpholine	960	480	5.30
Diethylamine	480	550	3.07
Butylamine	360	90	3.40
Methanol	3	16	—

**Scheme 2.**

In the presence of amines the decay rate of the DPBP ring-opened form was very much accelerated, depending upon the species and concentrations. After short-period irradiation of DPBP in solution at 313 nm, an amine solution was added, and the spectral change of the irradiated solution was followed at 410 nm at 20 °C. The second-order rate constants were calculated by analyzing the initial 10% decrease in absorbance as a reaction of the ring-opened form with amines or methanol. Concentrations of the DPBP ring-opened form were calculated from its molar absorption coefficient ( $\epsilon$ ) (see Experimental). The rate constants for quenching of the DPBP ring-opened form by typical amines and methanol were determined in 1,4-dioxane and cyclohexane, as listed in Table 2, where  $pK_b$  values of the amines are also listed. The ring-opened forms of DPBP consist of four isomers (Scheme 2).<sup>3</sup> The species with a lifetime in the minute-to-hour range can be assigned to the *EE* isomer in analogy with 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.<sup>7</sup> The rate constants can be ascribed to those for addition of the amines to the *EE* isomer of the DPBP ring-opened forms. Table 2 shows that the addition of amines is faster in 1,4-dioxane than in cyclohexane. Plot of logarithms of the rate constants against  $pK_b$  gave a straight line except for morpholine, showing that the more basic, the more reactive the amines. These facts indicate that the quenching of the ring-opened form is a nucleophilic addition of amines to the enone skeleton. Table 2 also shows that the amines are much more reactive with the ring-opened form than methanol. Taking into account that the methanol adduct thermally reverts more easily to the original components than do the amine adducts (see Ex-

**Table 3.** Apparent Quantum Yields for Addition of Amines (A) to DPBP

Amine	Apparent quantum yield		
	In 1,4-dioxane [A] = 2 mM	In cyclohexane [A] = 2 mM	In cyclohexane [A] = 0.2 M
Piperidine	0.45	0.30	0.50
Morpholine	0.30	0.18	0.51
Diethylamine	0.13	0.10	0.47
Butylamine	0.08	0.04	—

**Figure 2.** Relationship between the apparent quantum yield and the addition rate constant.

perimental), the addition of amines to the DPBP ring-opened form is more exothermic and lower in activation energy than the methanol addition.

The photochemical addition of amines to DPBP has been shown not to be a simple photochemical reaction but to be a photochemical and thermal two-step reaction. However, it is important to determine photochemical efficiency (apparent quantum yield) of the reaction, since this reaction is initiated with absorption of photons by DPBP. As an example, a solution of DPBP and morpholine in 1,4-dioxane or cyclohexane was irradiated at 313 nm, and the formed adduct and the remaining DPBP were analyzed quantitatively with HPLC at low conversion (within 10%) of DPBP. The amount of the remaining DPBP was also determined by spectral change at 333 nm since the absorbance at this wavelength is exclusively due to DPBP. The apparent quantum yields ( $\Phi_a$ ) for adduct formation in the presence of 2 mM of amines are dependent upon the amines and higher in 1,4-dioxane than in cyclohexane, as listed in Table 3. It is noticeable that the amine and solvent dependence of  $\Phi_a$  is quite similar to that observed in the addition rate measurements. In Figure 2 is depicted the relationship between  $\Phi_a$  and the rate constant. Figure 2 shows that  $\Phi_a$  is well correlated with the addition rate constant; the efficiency of adduct formation is controlled by the addition rate.

In the presence of 0.2 M of amines,  $\Phi_a$ 's were higher than those in the presence of 2 mM of amines, and reached approximately 0.5 independently of the amines employed. Comparison of the decay and quenching data in Tables 1 and 2 indicates that the observed ring-opened form is almost completely quenched by the 0.2 M amines. Consequently,  $\Phi_a$  of 0.5 corre-

sponds to the quantum yield for formation of the ring-opened *EE* form, the most long-lived isomer. Also, this value is assumed to be a minimal quantum yield for photocleavage of DPBP, which generates the short-lived *EZ* and other forms as well as the *EE* form. To the best of our knowledge, this is the first report on the quantum yield for ring opening of 2*H*-1-benzopyran analogs.

## Experimental

Melting points are uncorrected. UV-vis absorption spectra were measured with a JASCO U-560 spectrophotometer. Proton NMR spectra were recorded with a JEOL JNM-GSX270N (270 MHz) spectrometer. Precise-mass and ESI-mass spectra were measured with a Hitachi M80B and a Thermo Quest Finnigan AQA mass spectrometer, respectively.

**Photoaddition of Amines.** A solution of 23 mg of DPBP and 1 mL of morpholine in 30 mL of cyclohexane in a quartz cylindrical cell was irradiated for 20 min under nitrogen atmosphere using a 500-W high-pressure mercury lamp with Kenko U-340 glass filter. These irradiation operations were performed two times. The reaction mixtures were combined, and the solvent and morpholine were removed under reduced pressure. The resulting oil was chromatographed on 5 g of silica gel using hexane-ethyl acetate (4:1 by volume) as eluent. Removal of the solvent left 62 mg of white residue, which was crystallized from hexane to give 36 mg of a white solid, whose structure was assigned as 1,1-diphenyl-3-(2-hydroxyphenyl)-3-morpholino-1-propene on the basis of its characteristic spectra; mp 55–56 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.44–2.57 (m, 2H), 2.6–2.8 (broad s, 2H), 3.6–3.8 (m, 4H), 4.22 (d, 1H, *J* = 10.5 Hz), 6.37 (d, 1H, *J* = 10.5 Hz), 6.74–6.92 (m, 3H), 7.1–7.3 (m, 8H), 7.4–7.5 (m, 3H); precise-MS: *m/e* found, 371.1892; calcd for C<sub>25</sub>H<sub>25</sub>NO<sub>2</sub>, 371.1885.

Photoaddition of other amines to DPBP were conducted under similar conditions. Piperidine adduct: mp 129–131 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.40–1.70 (m, 6H), 2.30–2.60 (m, 4H), 4.28 (d, 1H, *J* = 10.0 Hz), 6.38 (d, 1H, *J* = 10.0 Hz), 6.70–6.85 (m, 2H), 6.93 (d, 1H, *J* = 8.7 Hz), 7.10–7.20 (m, 3H), 7.20–7.30 (m, 5H), 7.30–7.45 (m, 3H); precise-MS: *m/e* found, 369.1992; calcd for C<sub>26</sub>H<sub>27</sub>NO, 369.2093. Butylamine adduct: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.87 (t, 3H, *J* = 7.3 Hz), 1.20–1.45 (m, 4H), 2.45–2.65 (m, 2H), 4.45 (d, 1H, *J* = 10.0 Hz), 6.30 (d, 1H, *J* = 10.0 Hz), 6.70–6.92 (m, 3H), 7.10–7.25 (m, 8H), 7.32–7.45 (m, 3H); precise-MS: *m/e* found, 357.2123; calcd for C<sub>25</sub>H<sub>27</sub>NO, 357.2093. Propylamine adduct: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.87 (t, 3H, *J* = 7.6 Hz), 1.40–1.50 (m, 2H), 2.40–2.60 (m, 2H), 4.45 (d, 1H, *J* = 10.0 Hz), 6.29 (d, 1H, *J* = 10.0 Hz), 6.70–6.90 (m, 3H), 7.10–7.25 (m, 8H), 7.35–7.45 (m, 3H); ESI-MS: *m/e* found, 344.2; calcd for [C<sub>24</sub>H<sub>25</sub>NO + H]<sup>+</sup>, 344.2. Diethylamine adduct: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.92 (t, 6H, *J* = 6.6 Hz), 2.45–2.60 (m, 2H), 2.70–2.85 (m, 2H), 4.79 (d, 1H, *J* = 10.5 Hz), 6.29 (d, 1H, *J* = 10.5 Hz), 6.75–6.85 (m, 2H), 7.10–7.35 (m, 12H); ESI-MS: *m/e* found, 358.2; calcd for [C<sub>25</sub>H<sub>27</sub>NO + H]<sup>+</sup>, 358.2. 2-Ethanolamine adduct: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.70–2.90 (m, 2H), 3.50–3.70 (m, 2H), 4.47 (d, 1H, *J* = 10.0 Hz), 6.32 (d, 1H, *J* = 10.0 Hz), 6.70–6.95 (m, 3H), 7.10–7.30 (m, 8H), 7.35–7.45 (m, 3H); ESI-MS: *m/e* found, 368.2; calcd for [C<sub>23</sub>H<sub>23</sub>NO<sub>2</sub> + Na]<sup>+</sup>, 368.2.

**Lifetimes of the DPBP Ring-Opened Form in Solution.** A solution (2 mL) of DPBP (1 × 10<sup>-4</sup> M) in a quartz cell was irradiated for 60 s at 20 °C by a 500-W high-pressure mercury lamp through U-340 glass filter. The decrease in absorbance at 410 nm was followed at 20 °C.

**Quenching Efficiency of the DPBP Ring-Opened Form by Amines.** Immediately after irradiation of a solution (2 mL) of DPBP (1 × 10<sup>-4</sup> M) in 1,4-dioxane or cyclohexane for 60 s at 20 °C by a 500-W high-pressure mercury lamp through U-340 glass filter, 10 μL of an amine (1 × 10<sup>-2</sup> M) solution was added to this solution, and the decrease in absorbance at 410 nm was followed at 20 °C.

**Apparent Quantum Yields for Reaction of DPBP and Amines.** A solution (2 mL) of DPBP (2 × 10<sup>-3</sup> M) and morpholine (0.2 M) in cyclohexane was placed in a quartz cell, deaerated by bubbling with N<sub>2</sub> for 15 min, and irradiated for 30 s by a 500-W high-pressure mercury lamp through Kenko UV-30 and U-340 glass filter. The number of photons absorbed by DPBP was determined by using fulgide in toluene as chemical actinometer.<sup>8</sup> The concentrations of the adduct and the remaining DPBP were determined by HPLC through a Merck LiChrosorb Si60 column eluting with ethanol–hexane (2:8 by volume).

A solution (2 mL) of DPBP (2 × 10<sup>-3</sup> M) and an amine (2 × 10<sup>-3</sup> M) was irradiated for 35 s under similar conditions. The absorbance of the solution at 333 nm, where  $\mathcal{E}$ 's of DPBP are 500 cm<sup>2</sup> mmol<sup>-1</sup> in cyclohexane and 350 cm<sup>2</sup> mmol<sup>-1</sup> in 1,4-dioxane, was measured every 5 s.

**Molar Absorption Coefficient of the DPBP Ring-Opened Form.** A solution of DPBP (1 × 10<sup>-4</sup> M) in acetonitrile was irradiated for 30 s by a 500-W high-pressure mercury lamp through U-340 glass filter. Immediately after measurement of the UV-vis absorption spectrum of the solution, 5 μL of morpholine was added to this solution. The concentrations of DPBP before and after these operations were determined by HPLC through a Merck LiChrosorb RP-18 column eluting with acetonitrile–water (95:5 by volume). The molar absorption coefficient of the DPBP ring-opened form was estimated to be 6600 cm<sup>2</sup> mmol<sup>-1</sup> at 410 nm in acetonitrile by assuming that all the ring-opened form observed with the absorption spectrum reacted with morpholine added.

**Thermal Stability of the DPBP-Amine Adducts.** Proton NMR spectra of some adducts were followed at 50 °C in CDCl<sub>3</sub>. The signals due to the amine adducts gradually decreased in intensity and those due to DPBP increased. A half amount of the diethylamine adduct reverted to DPBP in 40 h, a 25% amount of butylamine adduct in 200 h, and a less than 10% amount of morpholine adduct in 600 h.

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