Photochromism of 1,1-Diaryl-1-alkanols

Masaki MATSUI,* Michinori TSUGE, Katsuyoshi SHIBATA, and Hiroshige MURAMATSU
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-11

(Received November 17, 1993)

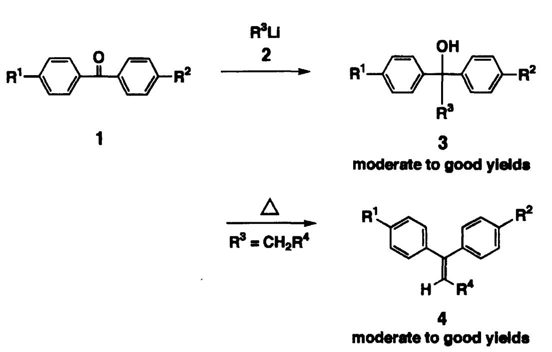
Synopsis. 1,1-Bis[4-(dimethylamino)phenyl]-1-alkanols were found to show photochromism.

Many photochromic compounds, such as triphenylmethane leuconitriles, fulgides, spiro compounds, 1,2-diarylethenes, azo compounds, indigo, and thioindigo, are known.[1] However, no information concerning the photochromism of 1,1-diaryl-1-alkanols has been reported. We describe here the photochromism of these compounds.

Results and Discussion

1,1-Diaryl-1-alkanols **3** and 1,1-diarylalkenes **4** were synthesized as shown in Scheme 1. The former were obtained by the reaction of diaryl ketones **1** with alkyllithium **2** in moderate to good yields. The latter were prepared by heating the corresponding **3** in good yields.

The results of the photochromism of 1,1-bis[4-(dimethylamino)phenyl]-1-pentanol (**3c**) on a silica-gel plate are shown in Fig. 1. When a drop of an acetone solution (ca. 1×10^{-2} mol dm^{-3}) of **3c** was put on the surface of the plate, followed by UV irradiation, the colorless component turned blue. The color intensity increased for 1.5 min, and then became constant under UV irradiation. Though the colored form gradually became colorless in the dark, it did not completely convert into a discolored one. Figure 2 shows the coloration and discoloration cycles of compound **3c**. The colored form remained even in the discoloration process by repeating the cycle. The photochromism of **3c**, depending on the amount of hydrochloric acid (**3c**: 0.18 mmol dm^{-3}, hydrochloric acid: 0.12 mmol dm^{-3}), was also observed in ethanol. In the solution, the speed of coloration and the discoloration processes was faster than that on a silica-gel plate.



Scheme 1. Synthesis of 1,1-diaryl-1-alkanols and 1,1-diarylalkenes.

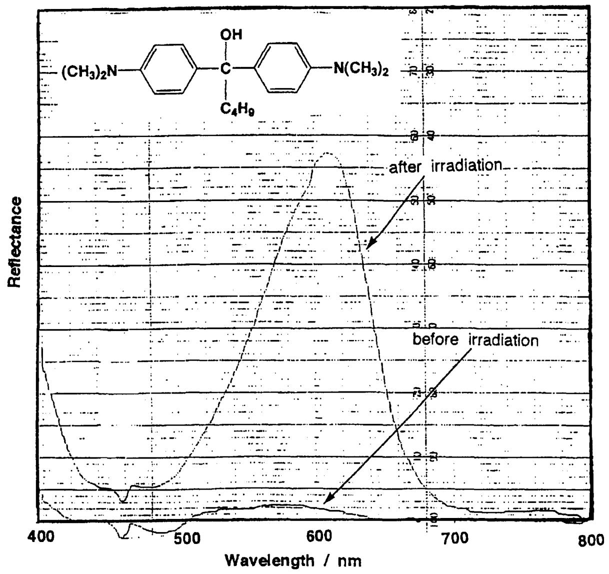


Fig. 1. Change in reflection spectrum of 1,1-bis[4-(dimethylamino)phenyl]-1-pentanol by UV irradiation.

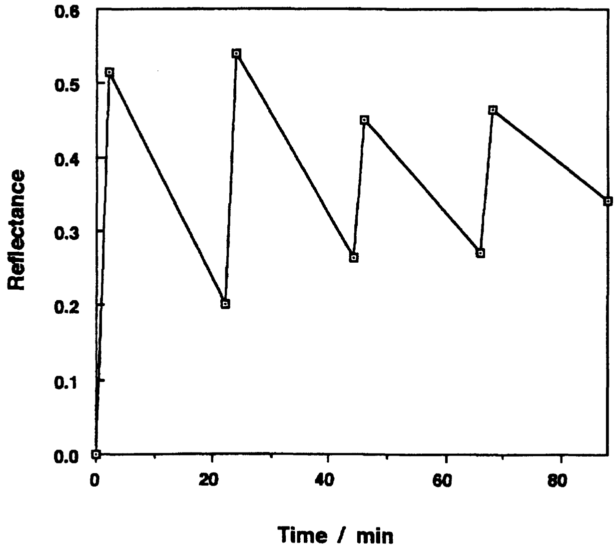
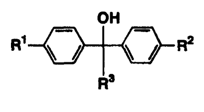


Fig. 2. Repetition test.

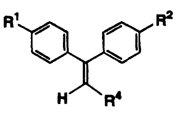
Photochromism and absorption bands of **3** and **4** are summarized in Table 1. No photochromism was observed on alumina and cellulose plates or in ethanol in the absence of an optimum amount of acid. Bis[4-(dimethylamino)phenyl] derivatives **3a**—**d**, having absorption maxima at around 620 nm in an acidic solvent, showed photochromism. Though the absorption band of **3e** in acetic acid was observed at 620 nm, this compound remained colorless under UV irradiation.

A plausible mechanism is shown in Scheme 2. 1,1-

Table 1. Photochromism and Absorption Spectral Data of 1,1-Diaryl-1-alkanols and 1,1-Diarylalkenes



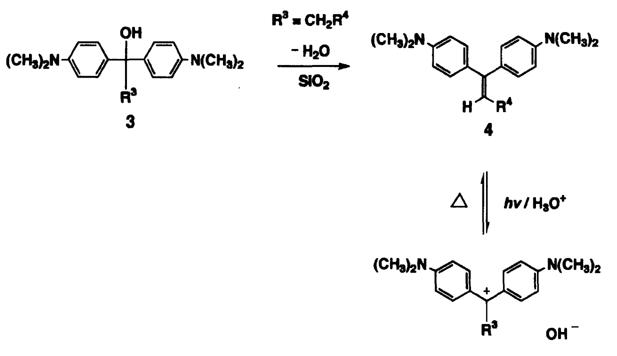
3



4

Compd	R^1	R^2	R^3	R^4	Photochromism		$\lambda_{max}(\varepsilon)$	
					on SiO_2[a]	in C_2H_5OH+HCl	C_2H_5OH	CH_3COOH
3a	$(CH_3)_2N$	$(CH_3)_2N$	CH_3	—	Yes	Yes	263(35500)	606(10900)[b]
3b	$(CH_3)_2N$	$(CH_3)_2N$	C_2H_5	—	Yes	Yes	281(44800)	620(19000)[b]
3c	$(CH_3)_2N$	$(CH_3)_2N$	n-C_4H_9	—	Yes	Yes	263(30000)	620(40000)
3c′	$(CH_3)_2N$	H	n-C_4H_9	—	No	No	261(16900)	258(18600)[c]
3d	$(CH_3)_2N$	$(CH_3)_2N$	$CH_2C_6H_5$	—	Yes	Yes[d]	264(22400)	638(24200)
3e	$(CH_3)_2N$	$(CH_3)_2N$	t-C_4H_9	—	No	No	263(27200)	620 (3100)
3f	$(CH_3)_2N$	$(CH_3)_2N$	C_6H_5	—	No[e]	No[e]	264(34700)	622(10500)
4a	$(CH_3)_2N$	$(CH_3)_2N$	—	H	Yes	Yes	293(22100)	607 (5700)
4b	$(CH_3)_2N$	$(CH_3)_2N$	—	CH_3	Yes	Yes	279(30800)	624 (9300)
4c	$(CH_3)_2N$	$(CH_3)_2N$	—	n-C_3H_7	Yes	Yes	283(34400)	617(47100)
4c′	$(CH_3)_2N$	H	—	n-C_3H_7	No	No	290(11100)	270(16400)[b]
4d	$(CH_3)_2N$	$(CH_3)_2N$	—	C_6H_5	Yes	Yes[d]	268(15900)	634(25000)

a) Silica gel 60 F254 (Merck). b) Ref. 2. c) Measured in ethanol–HCl. d) Very weak. e) Coloration was observed without UV irradiation.



Scheme 2. A plausible mechanism.

Diaryl-1-alkanols **3** are converted into the corresponding alkenes **4**, which give the carbonium ion **5** upon UV irradiation in the presence of a trace amount of acid and water. This proposal is supported by the following points: 1) both a small amount of acid and water exist on a silica-gel plate and in an ethanol solution; 2) not only 1,1-diaryl-1-alkanols **3a**—**d**, but also the corresponding alkenes **4a**—**d**, showed photochromism; 3) 1,1-diaryl-1-alkanols readily form the corresponding alkenes by a loss of water under acidic conditions;[2] and 4) no photochromism was observed in **3e**, which can not form 1,1-diaryl-1-alkene. In the case of **3f**, the alkanol converts to the triarylmethyl cation directly without UV irradiation.[3]

Experimental

Instruments. The melting points were measured with a Yanagimoto micro melting-point apparatus and were uncorrected. The NMR, mass, and UV spectra were taken on JEOL FT 270GX, Shimadzu QP-1000, and Hitachi 330 spectrometers, respectively.

Materials. 1,1-Diaryl-1-alkanols **3b**,[4] **3c**,[2] **3e**,[2] and **3f**,[5] were synthesized as described in the literature. 1,1-Diaryl-1-alkanols **3a**, **3c′**, and **3d** were prepared according to a similar procedure.

1,1-Bis[4-(dimethylamino)phenyl]-1-ethanol (3a): Yield 63%; mp 119—121 °C; ^{1}H NMR ($CDCl_3$) δ=1.89 (s, 3H), 2.92 (s, 12H), 2.97 (s, 1H), 6.68 (d, J=8.9 Hz, 4H), 7.27 (d, J=8.9 Hz, 4H); MS (70 eV) m/z (rel intensity) 284 (M^+, 13), 266 (100), 251 (29), 222 (16).

1-[4-(Dimethylamino)phenyl]-1-pentanol (3c′): Yield 90%; mp oil; ^{1}H NMR ($CDCl_3$) δ=0.86 (t, J=7.2 Hz, 3H), 1.23—1.37 (m, 4H), 2.19 (t, J=7.2 Hz, 2H), 2.88 (s, 7H, overlapping 6H and 1H), 6.65 (d, J=8.9 Hz, 2H), 7.16—7.28 (m, 3H), 7.24 (d, J=8.9 Hz, 2H), 7.35—7.41 (m, 2H); MS (70 eV) m/z (rel intensity) 265 (M^+-H_2O, 71), 236 (100), 220 (15).

1,1-Bis[4-(dimethylamino)phenyl]-2-phenyl-1-ethanol (3d): Yield 58%; mp 187—189 °C; ^{1}H NMR ($CDCl_3$) δ=2.92 (s, 13H, overlapping 12H and 1H), 3.56 (s, 2H), 6.66 (d, J=8.9 Hz, 4H), 6.92—6.96 (m, 2H), 7.14—7.16 (m, 3H), 7.25 (d, J=8.9 Hz, 4H); MS (70 eV) m/z (rel intensity) 343 (M^+-OH, 100), 269 (75), 148 (53), 119 (16).

1,1-Diarylalkenes (**4**) were synthesized by heating a solution (30 ml) (**a**—**c**, **c′**: ethanol, **d**: toluene) of 1,1-diaryl-1-alkanol **3** (1 mmol) until the starting material disappeared completely (ca. 2—4 h). After the reaction, the solvent was evaporated. The resulting precipitate was recrystallized from ethanol. Compound **4c′** was an oily product.

1,1-Bis[4-(dimethylamino)phenyl]ethane (4a): Yield 53%; mp 126—127 °C (lit,[6] 121—122 °C).

1,1-Bis[4-(dimethylamino)phenyl]-1-propene (4b): Yield 81%; mp 101—102 °C; ^{1}H NMR ($CDCl_3$) δ=1.77 (d, J=7.0 Hz, 3H), 2.92 (s, 6H), 2.97 (s, 6H), 5.94 (q, J=7.0 Hz, 1H), 6.64 (d, J=8.8 Hz, 2H), 6.74 (d, J=8.8 Hz, 2H), 7.07 (d, J=8.8 Hz, 2H), 7.12 (d, J=8.8 Hz, 2H); MS (70 eV) m/z (rel intensity) 280 (M^+, 100), 251 (10).

1,1-Bis[4-(dimethylamino)phenyl]-1-pentene (4c): Yield 96%; mp 45—47 °C; ^{1}H NMR ($CDCl_3$) $\delta=0.90$ (t, $J=7.3$ Hz, 3H), 1.38—1.52 (m, 2H), 2.12 (q, $J=7.3$ Hz, 2H), 2.92 (s, 6H), 2.97 (s, 6H), 5.86 (t, $J=7.3$ Hz, 1H), 6.64 (d, $J=8.9$ Hz, 2H), 6.73 (d, $J=8.9$ Hz, 2H), 7.06 (d, $J=8.9$ Hz, 2H), 7.13 (d, $J=8.9$ Hz, 2H); MS (70 eV) *m/z* (rel intensity) 308 (M^+, 57), 279 (82), 226 (100), 105 (69), 77 (31).

1-[4-(Dimethylamino)phenyl]-1-phenyl-1-pentene (4c′): Yield 98%; mp oil; ^{1}H NMR ($CDCl_3$) $\delta=0.88$ (t, $J=7.4$ Hz, 3H), 1.37—1.51 (m, 2H), 2.04 (q, $J=7.4$ Hz, 2H), 2.91 (s, 6H), 5.96 (t, $J=7.4$ Hz, 1H), 6.64 (d, $J=8.8$ Hz, 2H), 7.08—7.35 (m, 7H); MS (70 eV) *m/z* (rel intensity) 265 (M^+, 44), 236 (65), 210 (45), 148 (100).

1,1-Bis[4-(dimethylamino)phenyl]-2-phenylethene (4d): Yield 98%; mp 119—122 °C; ^{1}H NMR ($CDCl_3$) $\delta=2.96$ (s, 6H), 2.98 (s, 6H), 6.67 (d, $J=9.2$ Hz, 4H), 6.74 (s, 1H), 7.08 (d, $J=9.2$ Hz, 2H), 7.08—7.11 (m, 2H), 7.12—7.13 (m, 3H), 7.24 (d, $J=9.2$ Hz, 2H); MS (70 eV) *m/z* (rel intensity) 342 (M^+, 100).

References

1) H. Dürr and H. Bouas-Laurent, "Photochromism," Elselvier, Amsterdam (1990).

2) C. C. Barker and G. Hallas, *J. Chem. Soc.*, **1961**, 1395.

3) G. Hallas, D. E. Grocock, and J. D. Hepworth, *J. Soc. Dyers Colour.*, **86**, 200 (1970).

4) E. P. Kohler and R. H. Paatch, *J. Am. Chem. Soc.*, **38**, 1205 (1916).

5) V. Villiger and E. Kopetschni, *Ber.*, **45**, 2910 (1912).

6) P. Pfeiffer and R. Wizinger, *Justus Liebigs Ann. Chem.*, **46**, 132 (1928).