1834 © *1993 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***66****, 1834—1836(1993)* [Vol.66, No.6

Photochemical Ring Closure of 10,10′-Disubstituted 9,9′(10*H*,10′*H*)-Biacridinylidenes Followed by Dehyrogenation

Sachiko Yamada, Maki Kubo, Hiromi Fuke, Noriko Tsubaki, and Koko Maeda*
Department of Chemistry, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112

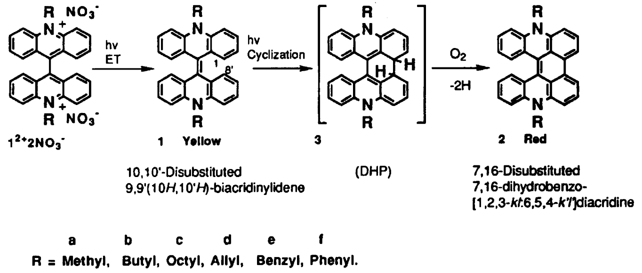
(Received December 7, 1992)

Synopsis. The photolysis of 10, 10′- disubstituted 9,9′(10*H*,10′*H*)-biacridinylidenes afforded the corresponding 7,16-dihydrobenzo[1,2,3-*kl*:6,5,4-*k′l′*]diacridines. The formation of photocyclized dihydrophenanthrene-type intermediates was confirmed spectroscopically.

We previously reported[1] that the photolysis of lucigenin, 10,10′-dimethyl-9,9′-biacridinium dinitrate ($\mathbf{1a}^{2+}2\mathrm{NO_3}^-$), gave a new red product, assumed to be 7,16-dimethyl-7,16-dihydrobenzo[1,2,3-*kl*:6,5,4-*k′l′*]-diacridine (**2a**). A mechanism was suggested that photoinduced electron-transfers from the counter anions to $\mathbf{1a}^{2+}$ reduce $\mathbf{1a}^{2+}$ into 10,10′-dimethyl-9,9′(10*H*,10′*H*)-biacridinylidene (**1a**), which is photocyclized into a dihydrophenanthrene (DHP)-type intermediate **3a**, and is subsequently dehydrogenated to give **2a** (Scheme 1).

Several reports[2,3] have described **1a** as showing no photocoloration, though other overcrowded bis-tricyclic ethylenes, such as 9,9′(10*H*,10′*H*)-bianthrylidene-10,10′-dione (BA) and 9,9′-bixanthenylidene (BX), exhibit photochromism (Chart 1). The photochromism is ascribed to the formation of two different photo-colored species: One is a DHP-type compound, analogous to **3a**. The presence of the DHP-type compound can be observed as a transient absorption only by using the method of flash photolysis at temperatures of around −75 °C.

We report here on the photolysis of **1a** into **2a** accompanied by a color change from yellow to red; we also confirm the structure of **2a** and the presence of a DHP-type intermediate **3a**. In this study we prepared several biacridinylidenes **1a**—**f** and investigated their photolysis.



Scheme 1.

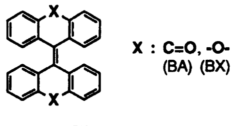


Chart 1.

Results and Discussion

Photolysis of 1 to Give Red Products 2. The photolysis of **1a**—**f** was carried out in deaerated benzene. All of the solutions turned red, thus showing a characteristic absorption band at around 520 nm, as **2a** did in a previous study.[1] As in the case of **1a**, **1b**—**f** underwent photolysis to give the corresponding red products **2b**—**f** (Table 1). The MS and ^{1}H NMR data of **2a**—**f** elucidated phenanthrene-type structures, as was assumed for **2a** (Table 2). Particularly in the ^{1}H NMR spectra, a low-field signal at about $\delta=7.8$ was assigned to protons at 3-H and 4-H in the phenanthrene moiety. The methylene protons on each N atom appear as nonequivalent signals, supporting the idea that ring closure occurs at the 1 and 8′ positions. In addition, aromatic protons were analyzed by a conventional decoupling method. The ^{13}C NMR spectra of **2a**—**f** also supported structures containing the phenanthrene ring.

Confirmation of the Presence of DHP-Type Intermediates 3. In order to clarify the formation of intermediates **3a**—**f**, the photolysis of **1a**—**f** in highly degassed (under 2×10^{-5} Torr (1 Torr≈133.322 Pa)) benzene at various temperatures between 13 and 40 °C was monitored by absorption spectroscopy. At a temperature higher than 30 °C, yellow solutions of **1a**—**f** occasionally turned green, then red. This suggested that a green intermediate was present. Figure 1a shows the spectral change upon the irradiation of **1f**. The intensity of the absorption band at 420 nm due to **1f** decreases along with the appearance of a new broad band at around 500—700 nm and an increase in the intensity of the new band. Two isosbestic points appeared at 380 and 460 nm, indicating that **1f** converts into a green intermediate. Upon admission of a small amount of air, the green solution turned red accompanied by a spectral change in the 450—700 nm region, finally affording the spectrum of **2f** (Fig. 1b). These facts indicate that a green intermediate is present during the course of the conversion of **1f** into **2f**. The structure of **3f** (Scheme 1) is assigned to the green intermediate, which is dehydrogenated into a phenanthrene-type product **2f** by O_2 in the air.

To further confirm the structure of **3** we tried to obtain the ^{1}H NMR spectrum of the green intermediates. The photolysis of **1** (**1a**, **1d**, and **1f**) was monitored by NMR spectroscopy. Upon the irradiation of **1** in degassed CD_2Cl_2, it was converted into a two-electron oxidation product $\mathbf{1}^{2+}$, which was probably formed

Table 1. The photolysis of 10,10′-Disubstituted 9,9′(10*H*,10′*H*)-biacridinylidenes **1a**—**f**

Substrate		Reaction time	Product	Yield[a]	Mp
	R	h		%	θ_m/°C
1a	CH_3	4	**2a**	50	324 (decomp)
1b	$(CH_2)_3CH_3$	4.5	**2b**	69	205.3—210.3
1c	$(CH_2)_7CH_3$	3.5	**2c**	50	c)
1d	$CH_2CH=CH_2$	1	**2d**[b]	47	221.0—222.0 (decomp)
1e	$CH_2C_6H_5$	1	**2e**	32[d]	271.0—276.0 (decomp)
1f	C_6H_5	8	**2f**	32[d]	c)

a) Isolated yield. b) Elemental analysis. Found: C, 87.85; H, 5.54; N, 6.31%. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42%. c) Not measured. d) Determined by ^{1}H NMR spectroscopy.

Table 2. MS and ^{1}H NMR Data of **2a**—**f**

	MS m/z (rel intensity/%)			^{1}H NMR δ[a]
	M$^+$	(M−R)$^+$	(M−2R)$^+$	
2a	384 (100)	369 (40)	354 (10)	7.85 (d, 2H, J=8.3 Hz and dd, 2H, J=8.0, 1.5 Hz, ArH), 7.44 (dd, 2H, J=8.3, 7.5 Hz, ArH), 7.21 (ddd, 2H, J=8.3, 7.5, 1.5 Hz, ArH), 7.06 (dd, 2H, J=8.3, 1.0 Hz, ArH), 6.83 (d, 2H, J=7.5 Hz, ArH), 6.70 (ddd, J=8.0, 7.5, 1.0 Hz, ArH), 3.52 (s, 6H, >NCH_3)
2b	468 (40)	411 (30)	354 (100)	7.80 (d, 2H, J=8.1 Hz and dd, 2H, J=8.1, 1.4 Hz, ArH), 7.39 (dd, 2H, J=8.1, 8.1 Hz, ArH), 7.18 (ddd, 2H, J=8.0, 7.1, 1.4 Hz, ArH), 7.01 (dd, 2H, J=8.0, 1.0 Hz, ArH), 6.81 (d, 2H, J=8.1 Hz, ArH), 6.64 (ddd, 2H, J=8.1, 7.1, 1.0 Hz, ArH), 4.06 (dt, 2H, J=19.9, 5.7 Hz, one of >NCH_2–), 3.90 (dt, 2H, J=19.9, 5.7 Hz, the other of >NCH_2–), 1.96 (m, 4H, –CH_2–), 1.59 (sext, 4H, J=8.0 Hz, –CH_2–), 1.10 (t, 6H, J=8.0 Hz, –CH_3)
2c	580 (25)	467 (10)	354 (100)	[b]7.81 (d, 2H, J=8.0 Hz and dd, 2H, J=8.0, 1.6 Hz, ArH), 7.39 (dd, 2H, J=8.0, 8.0 Hz, ArH), 7.16 (ddd, 2H, J=8.4, 7.6, 1.6 Hz, ArH), 7.00 (dd, 2H, J=8.4, 1.0 Hz, ArH), 6.80 (d, 2H, J=8.0 Hz, ArH), 6.65 (ddd, 2H, J=8.0, 7.6, 1.0 Hz, ArH), 4.08 (dt, 2H, J=19.1, 5.2 Hz, one of >NCH_2–), 3.88 (dt, 2H, J=19.1, 5.2 Hz, the other of >NCH_2–), 1.94 (quint, 4H, J=5.2 Hz, –CH_2–), 1.55—1.25 (m, 20H, –CH_2–), 0.92 (t, 6H, J=7.0 Hz, –CH_3)
2d	436 (2)	395 (4)	354 (100)	7.75 (d, 2H, J=8.1 Hz, ArH), 7.74 (dd, 2H, J=7.8, 1.3 Hz, ArH), 7.31 (dd, 2H, J=8.1, 8.0 Hz, ArH), 7.08 (ddd, 2H, J=8.7, 7.5, 1.3 Hz, ArH), 6.93 (dd, 2H, J=8.7, 1.1 Hz, ArH), 6.75 (d, 2H, J=8.0 Hz, ArH), 6.59 (ddd, 2H, J=7.8, 7.5, 1.1 Hz, ArH), 6.04 (ddt, 2H, J=16.2, 10.8, 3.2 Hz, –$CH_2C\underline{\underline{H}}=CH_2$), 5.26 (dd, 2H, J_{cis}=10.8 and J_{gem}=2.0 Hz, –$CH=C\underline{\underline{H}}_2$), 5.12 (dd, 2H, J_{trans}=16.2 and J_{gem}=2.0 Hz, –$CH=C\underline{\underline{H}}_2$, 4.72 (dd, 2H, J=19.4, 3.2 Hz, one of >NCH_2–), 4.46 (dd, 2H, J=19.4, 3.2 Hz, the other of >NCH_2–)
2e	536 (Trace)	445 (2)	354 (100)	7.89 (dd, 2H, J=8.1, 1.5 Hz, ArH), 7.84 (d, 2H, J=8.1 Hz, ArH), 7.40—7.28 (m, 12H, ArH), 7.08 (ddd, 2H, J=8.3, 7.2, 1.5 Hz, ArH), 6.87 (dd, 2H, J=8.3, 1.1 Hz, ArH), 6.70 (ddd, 2H, J=8.1, 7.2, 1.1 Hz, ArH), 6.66 (d, 2H, J=7.9 Hz, ArH), 5.47 (d, 2H, J=18.2 Hz, one of >NCH_2–), 5.19 (d, 2H, J=18.2 Hz, the other of >NCH_2)
2f [c]				[b]7.87 (dd, 2H, J=7.6, 1.8 Hz, ArH), 7.67 (6H, ArH),[d] 7.58 (d, 2H, J=7.6 Hz, ArH), 7.44 (4H, ArH),[d] 7.32 (2H, ArH), 7.17 (dd, 2H, J=8.1, 7.6 Hz, ArH), 6.82 (dd, 2H, J=6.8, 1.4 Hz, ArH), 6.29 (dd, 2H, J=8.1, 1.4 Hz, ArH), 6.17 (d, 2H, J=7.6 Hz, ArH)

a) Solvent: **2a**, **2d**, **2e**, and **2f** in CD_2Cl_2, **2b** and **2c** in $CDCl_3$. b) Assigned from the spectrum of the mixture with the starting material **1**. c) Not measured. d) Overlapped by signals of **1f**.

by the oxidation of **1** by Cl• generated from the solvent molecule under irradiation. No red product **2** was found. On the other hand, in degassed C_6D_6 **1** turned red via green upon irradiation. However, the ^{1}H NMR spectrum did not show any signals assignable to **3** at any period. All of the signals were assigned to **1** and/or **2**. These facts explained the following: 1) Most of **3** produced upon irradiation was readily dehydrogenated by a trace amount of oxygen remaining in the solution while measuring its NMR spectrum and 2) due to the

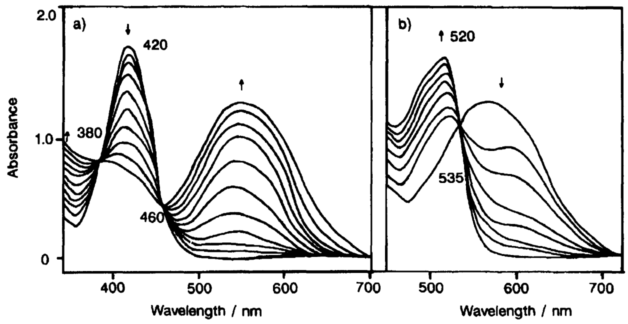


Fig. 1. a) Absorption spectral change of yellow **1f** to green **3f** upon irradiation in a degassed benzene solution with time; before irradiation and every 1 min upon irradiation. b) Absorption spectral change of green **3f** to red **2f** upon the admission of air into a benzene solution of **3f** with time.

low solubility of **1** into the solvent the concentration of **3** in the reaction mixture was under the detection limit of ^{1}H NMR spectroscopy.

In the case of the 1,8′-dimethyl derivative of BA, its DHP intermediate is sufficiently stable to be detected by NMR spectroscopy.[2b)] However, the photolysis of the 1,8′-dimethyl derivative of **1a**, 1,8′,10,10′-tetramethyl-9,9′(10*H*,10′*H*)-biacridinylidene (**4**), did not give both of the corresponding DHP intermediate and the red product.

Although the NMR spectrum of **3** has not been obtained, the results of an absorption spectroscopic investigation and the formation of **2** by O_2 strongly confirmed the presence of the DHP-type intermediate upon the photolysis of **1** into **2**.

Experimental

The melting points were measured with a Yanaco MP-3 micro melting point apparatus and are uncorrected. The IR spectra were measured with a JASCO A-302 infrared spectrophotometer. The absorption spectra were recorded on a Shimadzu UV240 spectrophotometer. The ^{1}H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were obtained with a JEOL JNM-GX 270 spectrometer. Me_4Si for ^{1}H NMR and CD_2Cl_2 or $CDCl_3$ for ^{13}C NMR were used as internal standards. The mass spectra were run on a Hitachi RMU 6MG spectrometer.

Starting Materials. 10,10′-Disubstituted 9,9′(10*H*,10′*H*)-biacridinylidenes, **1a**—**e**, were prepared from 9(10*H*)-acridone (purchased from Aldrich) according to a method of Amiet.[4)] 10,10′-Diphenyl-9,9′(10*H*,10′*H*)-biacridinylidene (**1f**)[5)] and 1,8′,10,10′-tetramethyl-9,9′(10*H*,10′*H*)-biacridinylidene (**4**)[6)] were prepared as reported by Gleu and coworkers.

Photolysis of 10,10′-Disubstituted 9,9′(10*H*,10′*H*)-Biacridinylidenes, 1a—f into 7,16-Disubstituted 7,16-Dihydrobenzo[1,2,3-*kl*:6,5,4-*k′l′*]diacridines, 2a—f. The irradiation of **1a**—**f** was performed in benzene (ca. 3×10^{-4} mol dm^{-3}) by a 400-W high-pressure mercury lamp or by a 500-W xenon lamp without a filter at 30 °C in a thermostatically controlled bath under N_2 or Ar. The solution turned red within several hours. After the resulting solutions were concentrated, the red products **2a**—**f** were isolated by chromatography and recrystalized from benzene.

Spectrometry. Each benzene solution of **1a**—**f** was introduced into a long-necked square 10-mm path-length quartz cell for a UV-vis analysis or into a 3-mm ϕ cell for an NMR analysis, then degassed by repeated freeze-pump-thaw cycles. Each sample was irradiated with a 400 W high-pressure mercury lamp at temperatures within 13—40 °C in a thermostatically controlled bath while being monitored spectroscopically.

We thank Professor Mamoru Ohashi, the University of Electro-Communications for measuring the mass spectra.

References

1) K. Maeda, T. Miyahara, T. Mishima, S. Yamada, and Y. Sano, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 441.

2) a) R. Korenstein, K. A. Muszkat, and E. Fischer, *J. Chem. Soc., Perkin Trans. 2*, **1977**, 564; b) R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv, Chim. Acta*, **53**, 2102 (1970); c) E. Fischer, *Rev. Chem. Intermed.*, **5**, 393 (1984), and references cited there in.

3) G. Kortüm, *Ber. Bunsen-Ges. Phys. Chem.*, **78**, 391 (1974).

4) R. G. Amiet, *J. Chem. Educ.*, **59**, 163 (1982).

5) K. Gleu and R. Schaarschmidt, *Ber.*, **73**, 909 (1940).

6) K. Gleu and S. Nitzcka, *J. Prakt. Chem.*, **153**, 200 (1939).