Construction and Transformation of 10,11-Dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-imines by Photoinduced Electron Transfer

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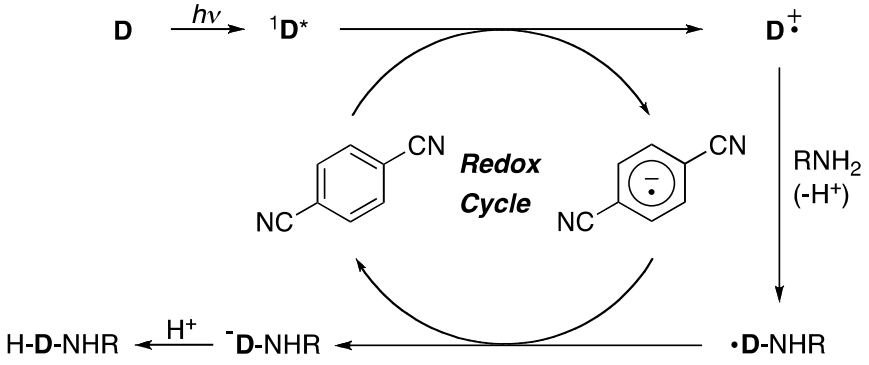
(Accepted August 5, 2013)

Abstract The photoamination of 5*H*-dibenzo[*a,d*]cyclohepten-5-ol (**1a**) and 5-methoxy- and 5-acetoxy-5*H*-dibenzo[*a,d*]cycloheptene (**1b** and **1c**) with ammonia and amines and the subsequent cyclization with AcOH gave the *N*-unsubstituted or *N*-substituted 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-imines (**2**). The *N*-methyl analog of **2** was transformed to the *N*-formyl analog (**2j**) by 9,10-dicyanoanthracene (DCA)-photosensitized reaction under O_2. Moreover, DCA-photosensitization of the *N*-isopropyl analog (**2c**) gave the unsubstituted analog (**2a**). The alkylation of **2a** was performed by the treatment with *n*-BuLi followed by the reaction with alkyl bromide.

Keywords [Photoamination, Cycloheptenimines, Electron transfer, Cyclization]

1 Introduction

A direct photoamination has provided a powerful synthetic tool, since the photoamination proceeds under mild conditions by a mechanism involving nucleophilic addition of amines to the cation radicals of substrates D ($D^{+\cdot}$) generated by photoinduced electron transfer from D to *p*-dicyanobenzene (DCB) acting as an electron acceptor (Scheme 1). The photoamination has been applied to the amination of a variety of electron-donating substrates[1~7] and the construction of heterocycles such as benzylisoquinolines, isopavines, and aporphines.[8~10]



Scheme 1 Photoamination via Electron Transfer

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Dibenzo[*a,d*]cycloheptenimines such as MK-801 are interesting synthetic targets because they have biologically activity as anticonvulsant and neuroprotective agents.[11,12] The general approach to the construction of the dibenzo[*a,d*]cycloheptenimine moiety is a thermal transannular addition of hydroxyamine to alkenes.[13~15] However, this process requires the basic condition for the addition reaction and the removal of hydroxy group. Direct intramolecular amination by lanthanide catalyst under mild conditions was reported.[16] We also reported to synthesis of dibenzo[*a,d*]cycloheptenimines under mild conditions using the photoamination of 5*H*-dibenzo[*a,d*]cyclohepten-5-ol (**1a**).[17] In order to develop more efficient synthetic method of the *N*-unsubstituted or *N*-substituted 10,11-dihydro-dibenzo[*a,d*]cyclohepten-5,10-imines (**2**), this paper describes the photoamination of 5-methoxy- and 5-acetoxy-5*H*-dibenzo[*a,d*]cycloheptene (**1b** and **1c**) and a convenient construction and transformation of **2**.

2 Experimental

2.1 Instruments

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 250 MHz and 62.9 MHz, respectively. Chemical shifts were reported in ppm relative to TMS as an internal standard. Mass spectra were operated at an ionization voltage of 70 eV. The fluorescence spectra were measured by single-photon counting method. The oxidation potentials were measured by cyclic voltummetry for an MeCN solution containing Et_4NBF_4 (0.1 mol dm^{-3}) as a scan rate of 0.5 V s^{-1} as a potentiostat and function generator using $Ag/AgNO_3$ as a reference electrode.

2.2 Preparation of 1.

5*H*-Dibenzo[*a,d*]cyclohepten-5-ol (**1a**) was prepared in 94% yield from the reduction of 5*H*-dibenzo[*a,d*]cyclohepten-5-one (90 mmol) with $NaBH_4$ (45 mmol) in ethanol (300 ml) at room temperature. Compounds **1b** and **1c** were prepared by refluxing **1a** (5 mmol) for 1 h in MeOH (30 ml)-Ac_2O (1 ml) and Ac_2O (10 ml), respectively. The spectral data of **1a** was shown in the previous report.[17]

5-Methoxy-5*H*-dibenzo[*a,d*]cycloheptene (1b). Yield 100%. ^{1}H NMR δ = 3.42 (3H, br s), 4.99 (1H, s), 7.06 (2H, s), 7.16-7.60 (8H, m); ^{13}C NMR δ = 57.40, 76.67, 122.22, 126.12, 127.66, 128.31, 128.69, 131.57, 131.67, 124.68, 139.20. HRMS Found: *m/z* 222.1035. Calcd for $C_{16}H_{14}O$: M, 222.1045.

5-Acetoxy-5*H*-dibenzo[*a,d*]cycloheptene (1c). Yield 87%. ^{1}H NMR δ = 2.84 (3H, br s), 4.77 (1H, s), 7.15 (2H, s), 7.22-7.36 (6H, m), 7.54 (2H, d, *J* = 7.5 Hz); ^{13}C NMR δ = 21.04, 76.75, 122.22, 126.12, 128.36, 128.69, 130.89, 139.19, 169.44. HRMS Found: *m/z* 250.0947. Calcd for $C_{17}H_{14}O_2$: M, 250.0994.

2.3 Synthesis of 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten- 5,10-imines 2.

The photoaminations of **1** were carried out by external irradiation of a deaerated MeCN-H_2O (9:1 v/v, 80 ml) solution containing **1** (4 mmol), DCB (4 mmol), and an amine (40 mmol) by a high-pressure mercury lamp through a Pyrex filter for 8 h. After the evaporation of the solvents, the photolysates were heated in AcOH (20 ml) at refluxing temperature for 5 h or in AcOH-H_2O (4:1 v/v, 20 ml) at 100 ˚C for 8 h. The reaction mixtures were neutralized by an aqueous $NaHCO_3$ solution and extracted with $CHCl_3$ to isolate **2**. Compounds **2** were shown in Scheme 2. The spectral data of **2b**, **2c**, **2e**, and **2f** were shown in the previous report.[17]

10,11-Dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-imine (2a). ^{1}H NMR δ = 2.60 (1H, d, *J* = 16.9 Hz), 3.29 (1H, dd, *J* = 16.9, 5.5 Hz), 4.61 (1H, d, *J* = 5.5 Hz), 4.86 (1H, s), 6.83-7.27 (m, 8H); ^{13}C NMR δ = 33.16, 58.97, 63.00, 119.86, 121.64, 123.89, 125.63, 126.75, 127.27, 130.35, 131.83, 141.52, 143.94, 149.37. HRMS Found: *m/z* 207.1041. Calcd for $C_{15}H_{13}N$: M, 207.1036.

***N-tert*-Butyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-imine (2d)**. ^{1}H NMR δ = 0.99 (9H, s),

2.70 (1H, d, *J* = 16.2 Hz), 3.39 (1H, dd, *J* = 16.2, 5.9 Hz), 4.69 (1H, d, *J* = 5.9 Hz), 4.97 (1H, s), 6.90-7.24 (8H, m); ^{13}C NMR δ = 28.33, 35.63, 53.66, 59.84, 64.00, 119.42, 121.31, 123.35, 125.42, 126.64, 126.75, 126.88, 130.31, 132.97, 142.91, 143.94, 150.05. HRMS Found: *m/z* 263.1622. Calcd for $C_{19}H_{21}N$: M, 263.1674.

Ethyl *N,N*-(10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-diyl)-2-aminopropanoate (2g). ^{1}H NMR δ = 1.39 (3H, t, *J* = 5.9 Hz), 1.43 (3H, t, *J* = 7.5 Hz), 2.54 (1H, d, *J* = 17.0 Hz), 3.37 (1H, dd, *J* = 17.0, 5.5 Hz), 4.07 (2H, q, *J* = 7.0 Hz), 4.17 (2H, q, *J* = 7.1 Hz), 4.57 (1H, d, *J* = 5.3 Hz), 4.90 (1H, s), 6.93-7.37 (8H, m); ^{13}C NMR δ = 14.09, 28.75, 29.95, 56.11, 56.84, 64.53, 65.62, 120.39, 121.79, 122.25, 124.89, 126.19, 127.35, 129.92, 132.63, 137.36, 141.75, 142.41, 147.24, 173.39. HRMS Found: *m/z* 307.1532. Calcd for $C_{20}H_{21}NO_2$: M, 307.1571.

Transformation of 2. DCA-photosensitized reaction of **2b** was performed by irradiation of an oxygen-saturated MeCN (20 ml) solution containing **2b** (0.5 mmol) and DCA (0.01 mmol) for 6 h. In the DCA-photosensitized reaction of **2c**, an MeCN (20 ml) solution containing **2c** (0.5 mmol) and DCA (0.01 mmol) was irradiated for 10 h. The alkylation of **2a** was performed according to the reported method[18] as follows: Into a dry tetrahydrofuran (THF) solution (3.5 ml) of **2a** (1.4 mmol) was added *n*-BuLi (1.25 ml) at -20 ˚C, and stirred for 90 min. The allyl bromide or benzyl bromide (1.5 mmol) in THF (3 ml) was added into the solution at 0 ˚C and stirred for 2 h, and at room temperature for additional 10 h. The spectral data of **2h** was shown in the previous report.[17]

***N*-Benzyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-imine (2i).** ^{1}H NMR δ = 2.55 (1H, d, *J* = 17.0 Hz), 3.33 (1H, dd, *J* = 17.0, 5.5 Hz), 3.61 (1H, d, *J* = 13.2 Hz), 3.72 (1H, d, *J* = 13.2 Hz), 4.30 (1H, d, *J* = 5.3 Hz), 4.62 (1H, s), 6.90-7.32 (13H, m); ^{13}C NMR δ = 30.90, 55.23, 62.57, 67.37, 121.02, 122.70, 124.71, 125.85, 126.77, 126.82, 126.96, 127.12, 128.23, 128.92, 129.90, 132.38, 138.79, 139.55, 142.46, 148.24. HRMS Found: *m/z* 297.1483. Calcd for $C_{22}H_{19}N$: M, 297.1517.

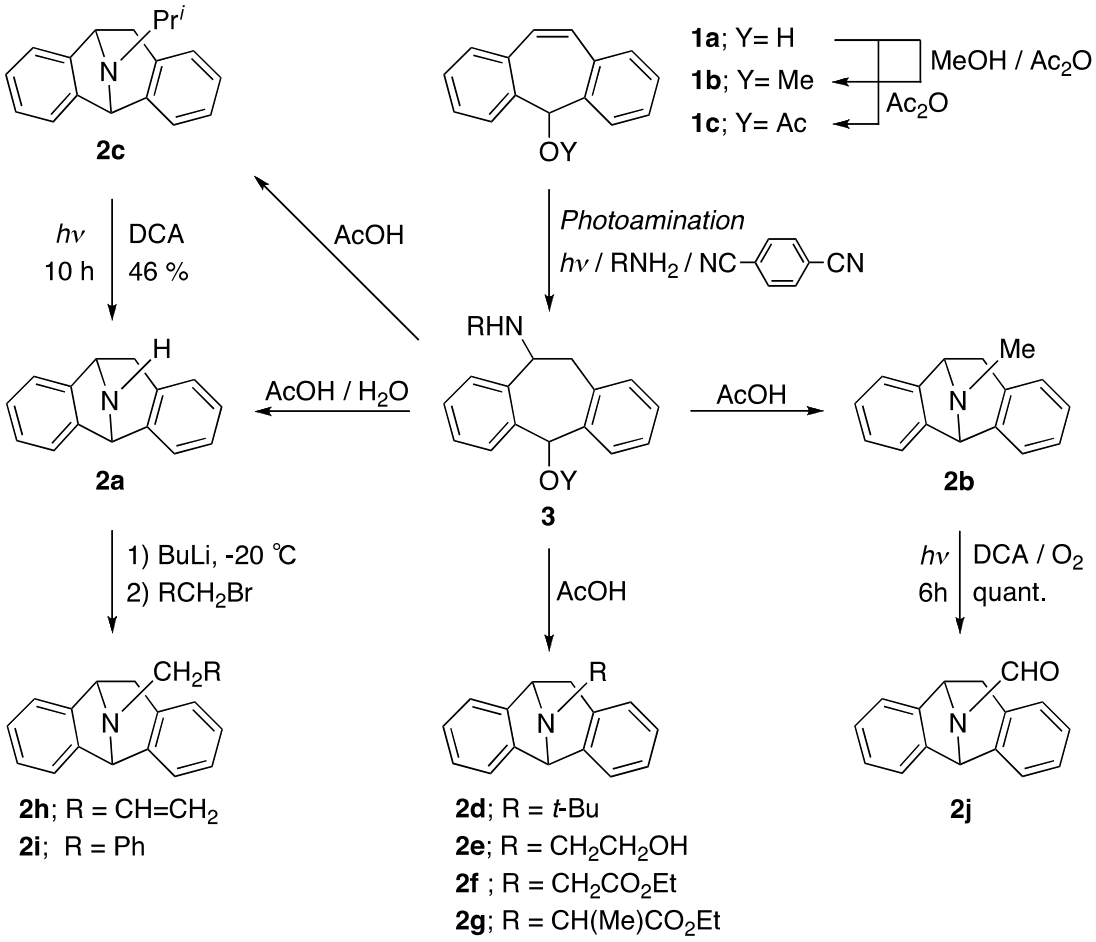
***N*-Formyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5,10-imine (2j)**. ^{1}H NMR δ = 2.72 and 2.85 (1H, d, *J* = 18.3 Hz), 3.40 and 3.53 (1H, dd, *J* = 16.8, 5.6 Hz), 5.25 and 5.74 (1H, d, *J* = 5.6 Hz), 5.54 and 6.06 (1H, s), 6.93-7.31 (8H, m), 8.20 and 8.25 (1H, s); ^{13}C NMR δ = 32.13 and 34.82, 54.97 and 58.26, 58.67 and 62.27, 119.61 and 120.15, 121.47 and 122.40, 123.09 and 124.22, 126.05 and 126.27, 127.27, 127.47, 127.60 and 127.78, 130.17 and 130.53, 131.15 and 131.65, 138.86 and 139.54, 139.74 and 139.95, 145.88 and 146.36, 157.08 and 157.82. HRMS Found: *m/z* 235.0978. Calcd for $C_{16}H_{13}NO$: M, 235.0960.

The PM3 calculation. The PM3 calculation was performed on a Silicon Graphics O2 work station using SPALTAN to give the structure with minimum heat formation.[19,20]

3 Results and Discussion

3.1 Preparation of 2.

As outlined in Scheme 2, the preparation of **2** was performed by the photoamination and the subsequent transannular reaction using **1a**,[17] **1b**, and **1c** as the starting materials. The aminated compounds of **1** (**3**) were prepared by irradiation of a deaerated MeCN-H_2O solution containing **1**, DCB, and RNH_2 for 8 h by a high-pressure mercury lamp. After the removal of solvents, the reaction mixtures were treated with AcOH at refluxing temperature (condition A) to give the *N*-substituted dibenzo[*a,d*]cycloheptenimines (**2b-g**). In the photoamination of the *N*-unsubstituted analog of **3** (**3a**), the irradiation was performed for an ammonia-saturated MeCN-H_2O solution containing **1** and DCB. The transformation of **3a** to **2a** was performed by heating in AcOH-H_2O (4:1) at 100 ˚C (condition B), because the treatment of **3a** under condition A gave the *N*-acetyl analog of **2a**.[17] After neutralization of the AcOH solutions, **2a-g** were extracted from the chloroform solution of the reaction mixtures with a dilute aqueous HCl solution. In every runs, the DCB was recovered from the chloroform solution in high yields. The results are summarized in Table 1.



Scheme 2 Synthesis and Transformation of Dibenzo[*a,d*]cycloheptenimines **2**

Table 1. Preparation of Dibenzo[*a,d*]cycloheptenimines (**2**) by the Photoamination of **1** Followed by the Cyclization with AcOH

Entry	**1**	RNH_2	Condition[a)]	Recovery (%)		**2** (Yield / %)[b)]	
				1	DCB		
1	**1a**	NH_3	B	23	85	**2a**	(19)
2	**1a**	$MeNH_2$	A	8	95	**2b**	(49)[c)]
3	**1b**	NH_3	B	0	94	**2a**	(80)
4	**1b**	$MeNH_2$	A	1	98	**2b**	(81)
5	**1b**	*i*-$PrNH_2$	A	0	91	**2c**	(79)
6	**1b**	*t*-$BuNH_2$	A	0	96	**2d**	(85)
7	**1b**	$HOCH_2CH_2NH_2$	A	0	96	**2e**	(63)
8	**1c**	$MeNH_2$	A	8	88	**2b**	(48)
9	**1c**	$EtOCOCH_2NH_2$	A	5	84	**2f**	(44)
10	**1c**	$EtOCOCH(Me)NH_2$	A	8	88	**2g**	(53)

a) For the cyclization of **3**. Condition A: refluxing in AcOH for 5 h; condition B: heating in AcOH-H_2O (4:1) at 100 ˚C for 8 h. b) Total yields based on **1** used. c) See ref. 17.

The comparison of runs 2, 4, and 8 shows that **1b** is a good starting material among **1a-c** for the formation of **2**. Especially, **2a** was prepared from **1b** in 80% yield, but the yield from **1a** was 19%. The present method for the preparation of **2a** is a simple method compared with the reported method via a Ritter reaction of 5-hydroxamino-5*H*-dibenzo[*a,d*]cycloheptene.[13)]

3.2 Transformation of 2.

The treatment of **2a** with BuLi at -20 ˚C followed by the addition of allylbromide and benzylbromide gave *N*-allyl and *N*-benzyl analogs (**2h** and **2i**) in 92% yields. Moreover, the transformation of the *N*-methyl analog (**2b**) to the *N*-formyl analog (**2j**) was performed by 9,10-dicyanoanthracene (DCA)-photosensitized reaction of an MeCN solution of **2b** under O_2 atmosphere. The DCA-photosensitized reaction of a deaerated MeCN of the isopropyl analog (**2c**) took place the dealkylation, resulting in the formation of **2a**.[21~25)]

3.3 Reaction Mechanism.

Table 2 shows the data which support the mechanistic consideration. Since the fluorescence of **1a-c** were quenched by DCB at nearly diffusional-controlled rates and since the free energy changes (ΔG) for the electron transfer from the excited singlet state of **1** to DCB were calculated to be negative by Rehm-Weller equation,[26)] the photoamination of **1a-c** was initiated by the electron transfer from the excited singlet state of **1** to DCB. Therefore, the photoamination proceeded according to Scheme 1 (D = **1a-c**).

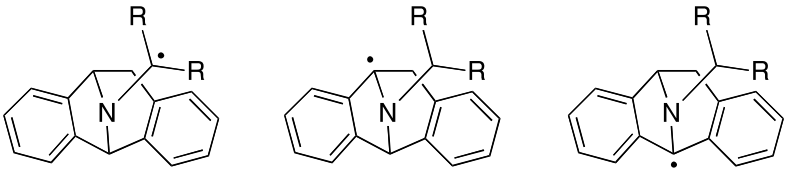
Table 2. Data for the Fluorescence Quenching

Fluoropher ($E_{1/2}$)[a)]	λ_{max}[b)]	τ_F[c)]	Quencher ($E_{1/2}$)	K_{SV}[d)]	k_Q[e)]	ΔG[f)]
V	nm	ns	V	$dm^3\ mol^{-1}$	$dm^3\ mol^{-1}\ s^{-1}$	kJ mol^{-1}
1a (1.30)	361	2.2	DCB (-1.91)	50	2.3×10^{10}	-27
1b (1.35)	345	2.2	DCB	38	1.4×10^{10}	-38
1c (1.34)	345	1.8	DCB	25	1.4×10^{10}	-39
DCA (-0.98)	436	15.3	**2b** (0.88)	142	0.9×10^{10}	-157
DCA			**2c** (0.82)	180	1.1×10^{10}	-150

a) The oxidation potentials for **1a-c** and **2b,c** and the reduction potentials for DCB and DCA were measured using $Ag/AgNO_3$ reference electrode. b) Emission maxima of fluorescence. c) Lifetimes of the fluorescence. d) Stern-Volmer constants for fluorescense quenching. e) Rate constants for the fluorescence quenching. f) Free energy change for the electron transfer from the excited state of fluoropher to the quencher calculated by the Rehm-Weller equation (ref. 26).

Also, the fluorescence quenching of DCA by **2b**,**c** suggests that the initiation process of the DCA-photosensitized reaction of **2b**,**c** is the electron transfer from **2b**,**c** to the excited singlet state of DCA ($^1DCA^*$), since the fluorescence quenching of DCA by **2b**,**c** occurred at nearly diffusional-controlled rates and since ΔG for the electron transfer from **2b**,**c** to $^1DCA^*$ were calculated to be largely negative by Rehm-Weller equation.[26)] The oxygenation of the radical (**4a**) derived from the deprotonation of $\mathbf{2b}^{+\cdot}$ caused the oxidation of methyl group of **2b**.[21~25)] Similarly the dealkylation of **2c** might proceed via **4b** formed by the deprotonation of $\mathbf{2c}^{+\cdot}$.[2)] No deprotonation from C-5 and C-10 positions in cycloheptenimine moiety in $\mathbf{2}^{+\cdot}$ occurred, probably because the rigid ring-structure prevents from the formation of a sp^2 planar carbon. The PM3-calculation for heat of formation was performed for the selected radicals (**4-6**) which

were produced by the deprotonation from α-carbon of the nitrogen atom in the cation radicals of **2**. The result that the heat formation of **4** were lowest among **4-6** was consistent with the fact of the deprotonation from $\mathbf{2}^{+\cdot}$ occurred selectively at alkyl group on nitrogen atom (Scheme 3).



4a; R= H (352)　**5a**; R= H (392)　**6a**; R= H (401)

4b; R= Me (267)　**5b**; R= Me (350)　**6b**; R= Me (359)

Scheme 3 Heat Formation of the Radicals (**4-6**) (kJ mol^{-1})

It is important to develop a clean synthetic process in order to prevent the chemical environmental pollution. Many organic syntheses, in general, have been achieved by the combination of the reactive species involving reactive substrates, reactive reagents, and/or reactive catalysts. In many cases, therefore, large amounts of materials which are not incorporated to final products remained as by-products, which will be emitted to atmospheres after the appropriate treatments. The present method via photoamination diminishes remarkably the amounts and sorts of reagents used for synthesis of **2** compared with the reported method.[8~10] Since a photon is a clean "reagent" which meets the above requirements, the photochemical method will provide a tool to develop clean synthetic process.

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