STUDIES ON NITROGEN-CONTAINING HETEROCYCLIC COMPOUNDS. SYNTHESES AND REACTIONS OF BENZO[*g*]QUINOLINE

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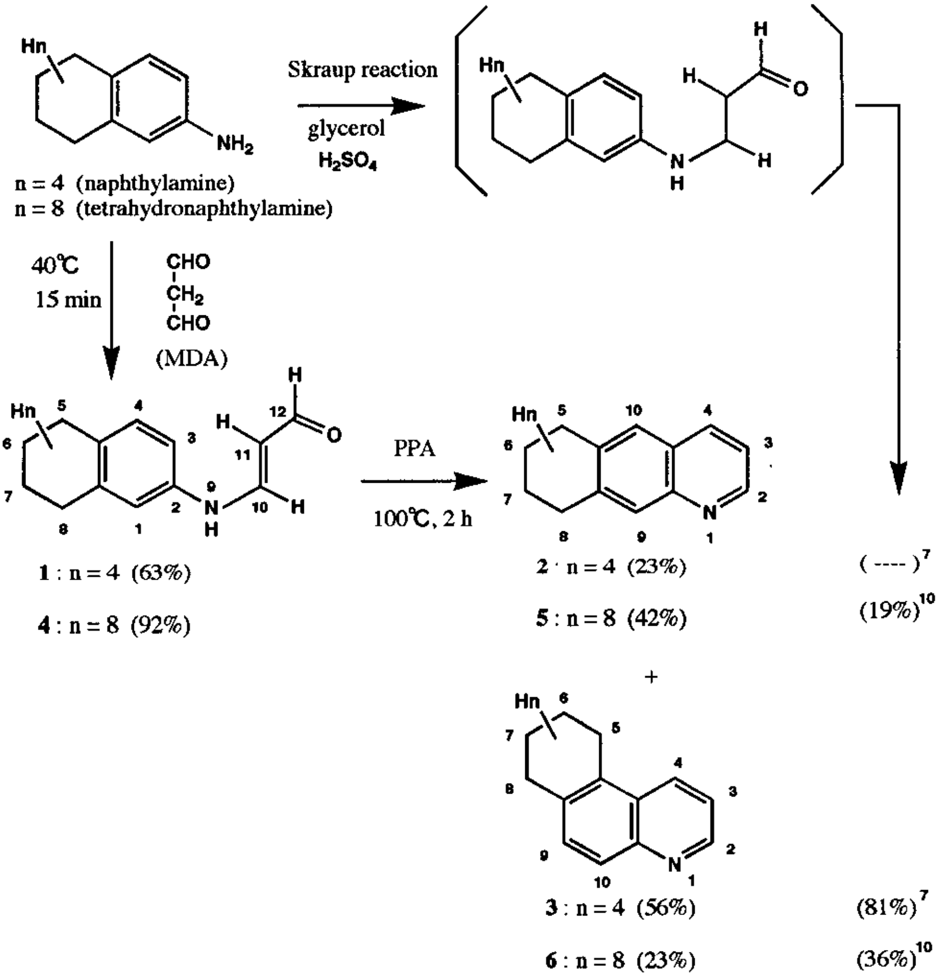
Abstract - The authors devised a new convinient synthesis of benzo[*g*]quinoline (**2**) through the condensation of β-naphthylamine with malondialdehyde (MDA) followed by cyclization in polyphosphoric acid. The reactivity of **2** toward *N*-oxidation, Reissert reaction and methylation with methylsulfinylmethyl carbanion was investigated.

Benzoquinoline has three condensed rings. Angular-type benzo[*f* and *h*]quinoline[1] has been studied extensively reactions of benzo[*f* and *h*]quinolines and its *N*-oxide with nucleophilic reagents appeared in our previous paper.[2] Little attention has been directed to the reactions of linear-type benzo[*g*]quinoline, only *N*-methylation,[3] phenylation by the Grignard reaction,[4] and dehydrogenative condensation[5] by pyridine *N*-oxide are described. This comes largely from the fact that synthetic methods hitherto reported were not suitable, as shown by poor yields and difficulty in product separation.[6] A modified synthesis of the benzo[*g*]quinoline skeleton and studies on *N*-oxidation, Reissert reaction and nucleophilic substitution with methylsulfinylmethyl carbanion are presented in the following.

SYNTHESIS OF BENZ0[*g*]QUINOLINE

The Skraup reaction of β-naphthylamine gives only benzo[*f*]quinoline,[7] while, the Combes reaction provides only the linearly annelated product, 2,4-dimethylbenzo[*g*]quinoline.[8] Although the details are not



Scheme 1

clear, differences in the reactivity of the respective intermediates may be the reason for this. The intermediate of the Skraup reaction has a saturated formyl group as the *N*-substituent, and that of the Combes reaction, an α,β-unsaturated carbonyl group. Taking this into consideration, the condensation reaction of β-naphthylamine was attempted using malondialdehyde (MDA) as the 1,3-dicarbonyl component. MDA has been prepared by hydrolysis of malondialdehyde bis(dimethylacetal) using 50% aqueous solution.[9] Treatment of β-naphthylamine with the MDA solution at 40 ℃ gave β-(2-naphthylamino)-acrolein (**1**) in 63% yield. The ring closure of **1** was examined under various conditions (Table 1). The reaction occurred best by treatment with polyphosphoric acid (PPA) at 100℃ for 2 h to afford the desired benzo[*g*]quinoline (**2**) in 23% yield, though with benzo[*f*]quinoline (**3**) formed in 56% yield. Thus, the preparation of **2** is possible in fair yield without difficulty of separation, but yield is not satisfactory.

Table 1. Reaction Conditions of the Cyclization of **1**

Reagents	Temp. (℃)	Time (min)	Product (**2**) (%)	Product (**3**) (%)	Recovery (%)	2-Naphthylamine (%)
H_2SO_4	100	20	0.5	1.0		
H_2SO_4	60	2	0.5	0.5		
H_2SO_4	r.t.[a]	15	1.6	1.1		
PPA	100	30	14	38	26	
PPA	100	120	23	56		
PPA	60	120	5	18	58	
HF-pyridine	r.t.[a]	180				50

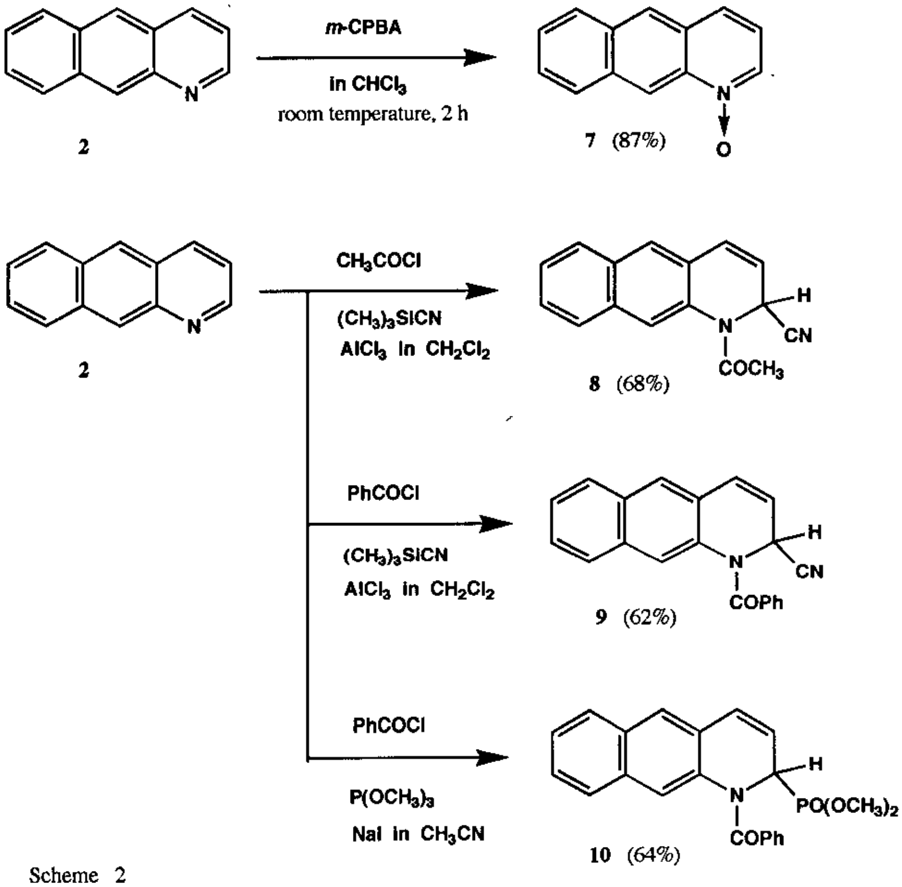
a) room temperature

Thus, the synthesis of **2** was conducted starting from 6-aminotetralin. 6-Aminotetralin reacted with MDA to give the tetrahydro analog of **1** (**4**) in high yield of 92%. Treatment of **4** with PPA under the same conditions gave an untractable mixture, which was shown by ^{1}H-nmr spectral analysis to contain the linear-type 5,6,7,8-tetrahydro-1-azaanthracene (**5**; 42.7%) and angular-type 5,6,7,8-tetrahydro-1-azaphenanthrene (**6**; 23%). Although the yield of **5** somewhat exceeded that of the Skraup reaction of 6-aminotetralin,[10] the separation of **5** from **6** was not possible at all. Thus it was considered that **2** could not be obtained *via* **5** through its dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[5]

REACTION OF BENZO[*g*]QUINOLINE

The oxidation of **2** with *m*-chloroperbenzoic acid under conditions the same as those for the oxidation of benzo[*f*]quinoline[11] afforded *N*-oxide (**7**) in 87% yield. Its structure was confirmed by the ^{1}H-nmr spectrum in which H_9 showed a paramagnetic shift due to the adjacent *N*-oxide group,[12] and H_2 and H_4 appeared at lower magnetic fields than that of **2**.

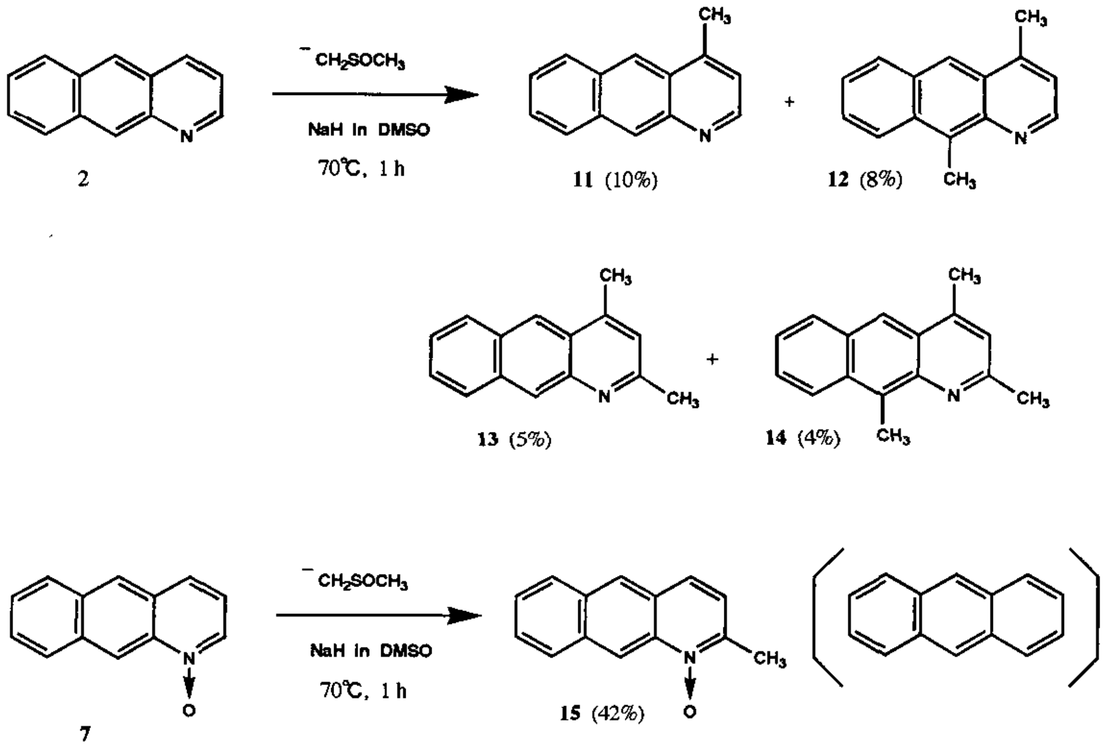
The Reissert reaction of **2** with acetyl or benzoyl chlorides and trimethylsilyl cyanide gave the corresponding 1,2-dihydro-type Reissert compounds (**8** and **9**). The Reissert type reaction of benzo[*f*]quinoline with benzoyl chloride and trimethyl phosphite gave α- and γ-phosphonates in essentially the same yields,[2a] while the same reaction of **2** provided only the α-phosphonate (**10**), whose structure was confirmed by the coupling constant J_{PH}=20.8 Hz. J_{PH} of 1,2-adducts ranged from 19 to 21 Hz, these values being considerably smaller than those for the 1,4-adducts for (23-26 Hz).[13]



Scheme 2

The reaction of **2** with methylsulfinylmethyl carbanion genarated from DMSO and sodium hydride was carried out under some conditions and the results are shown in Table 2. The reaction at room temperature for 1 h afforded only the 4-methyl derivative (**11**) in 54% yield. Under stronger conditions, the initially-formed **11** underwent further methylation to afford dimethyl (**12** and **13**[8]) and trimethyl derivatives (**14**). The formation of polymethylation products is noteworthy in view of the sole formation of a monomethylation product in the reaction of benzo[*f* or *h*]quinoline. The same reaction of the *N*-oxide (**7**) proceeded normally to give the 2-methyl *N*-oxide (**15**) as the sole product in moderate yield. Thus, the reaction of **7** differs from that of **2**, giving polymethylation products as well as benzo[*f* and *h*]quinoline *N*-oxides followed by the formation of deaza products through the ring cleavage of 1,2-dihydro intermediates and then re-cyclization.[14]

Table 3 shows the reactivity indexes of **2** as determined by PM3. The reaction of methylsulfinylmethyl carbanion which relatively low LUMO and stabilized by the delocalization of negative charges over the Csp^{2}-S-O system should be frontier-controlled. For such a reaction, superdelocalizability $Sr^{(-)}$ for



Scheme 3

Table 2. Reaction Conditions of the Methylation

Entry No.	Conditions	Starting Compound	Product (s) No.	Yield (%)
1	70 ℃ ,1 h	**2**	**11**	10
			12	8
			13	5
			14	4
2	70 ℃ ,15min	**2**	**11**	46
			12	6
3	r.t.[a] ,1 h	**2**	**11**	54
4	70 ℃ ,1 h	**7**	**15**	42
5	r.t.[a], 30min	**7**	**15**	54

a) room temperature

Table 3. Reactivity Indexes of Benzo[*g*]quinoline (**2**) from PM3 Calculations.[a]

Position (r)	Charge (ζ_r)	$Sr^{(-)}$	π - Density ($q_r(\pi)$)	Σ Yield [b] ($CH_3SOCH_2^-$)
1 (N)	- 0.059	0.279	1.080	
2	- 0.050 (1)	0.318 (4)	0.947 (1)	9%
3	- 0.153	0.300	1.026	
4	- 0.052 (2)	0.324 (1)	0.966 (2)	27%
10	- 0.067 (4)	0.320 (3)	0.994 (4)	
5	- 0.090	0.302	1.002	
6	- 0.096	0.301	0.996	
7	- 0.098	0.300	0.998	
8	- 0.087	0.303	0.997	
9	- 0.054 (3)	0.321 (2)	0.977 (3)	12%

a) Predicted orders of reactivity are given in parentheses.
b) Summation of the yields of products bearing methyl group at the designated position.

nucleophilic reactions has been shown to be the most appropriate reactivity. The reactivity order for the above methylation appears to be 4>9>2, which is consistent with superdelocalizability $Sr^{(-)}$ but not ζ or π-density [$q_r(\pi)$]. Although attack with the carbanion at position 10 would appear to occur from calculated $Sr^{(-)}$, no 10-methylation product was formed, possibly due to sterical hindrance from two *peri*-hydrogens (H_4 and H_5). Particularly in the initially-formed **11**, such formation would be quite difficult owing to the bulky 4-methyl group.

In contrast to the methylsulfinylmethyl carbanion with soft base character, the hard cyanide ion attacks the most positive C_2. In this case, the reaction should be charge-controlled, and *N*-acylation would enhance the reactivity owing to its electron-withdrawing effect. Thus, 2-cyanation in the Reissert reaction of **2** can be explained based on the charge density data in Table 3.

ACKNOWLEDGEMENT

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EXPERIMENTAL

^{1}H-Nmr spectra were recorded with a JEOL JNM GX-270 spectrometer with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given on the δ scale (ppm). The following abbreviations are used: s=singlet, d=doublet, dd=double doublet, m=multiplet, and br=broad. Ms were taken with a Hitachi GC-MS M-80 spectrometer. Molecular orbital calculations were carried out by using PM3 program on the geometry preliminarily optimized by MM2.

Preparation of Malondialdehyde in 1*N* HCl Solution

Malondialdehyde bis(dimethylacetal) (32.8 g, 0.2 mol) was added to 210 ml of 1*N* HCl. The flask was stoppered tightly and the suspension stirred at room temperature for several min until a homogeneous solution was obtained. The solution was then kept at 0 ℃ for 24 h. The resulting clear pale yellow solution (*ca.* 242 ml) was used to each reaction as 0.1 mol solution of malondialdehyde (MDA).

β-(2-Naphthylamino)-acrolein (1)

A solution of MDA (0.1 mol) in 1*N* HCl (242 ml) was added to a solution of β-naphthylamine (14.3 g, 0.1 mol) in 2% HCl (600 ml) at 40℃, and the mixture was stirred for 15 min. The reaction mixture was neutrarized with 28% NH_4OH and extracted with $CHCl_3$. The extract was dried over $MgSO_4$, the solvent was evaporated off, and the residue was recrystallized from acetone to give 12.4 g (63%) of **1** as coloress needles, mp 153-156℃. Ms: *m/z* 197 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 5.38 (dd, 1H, *J*=7.4, 2.0, H-11), 7.24 (dd, 1H, *J*=7.4, 2.4, H-3), 7.40 (m, 1H, H-10), 7.40~7.54 (m, 2H, H-6,7), 7.45 (d, 1H, *J*=2.4, H-1), 7.73~7.85 (m, 3H, H-4,5,8), 9.35 (dd, 1H, *J*=4.0, 2.0, CHO-12), 11.85 (br d, 1H, *J*=8.0, NH-9). *Anal.* Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.30; H, 5.56; N, 7.02.

Benzo[*g*]quinoline (2)

A mixture of **1** (2.0 g, 0.01 mol) and PPA (40 ml) was heated at 100 ℃ with stirring for 2 h. After cooling to room temperature, the reaction mixture was poured into H_2O (200 ml). The mixture was made alkaline with 28% NH_4OH and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were washed with water and dried over $MgSO_4$, and evaporated. The residue was chromatographed tree times on silica gel (CH_2Cl_2: Me_2CO = 20:1) to give 0.41 g (23%) of **2** as colorless needles (from hexane), mp 116-117 ℃ (lit.,[6b] mp 114 ℃, lit.,[5] mp 116.5-118.5 ℃), and 1.00 g (56%) of benzo[*f*]quinoline (**3**) as colorless needles (from hexane), mp 93-94 ℃ (lit.,[7] mp 93 ℃).

2: Ms: *m/z* 179 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 7.38 (dd, 1H, *J*=8.7, 4.0, H-3), 7.54 (m, 2H, H-6,7), 8.04 (m, 1H, H-5), 8.11 (m, 1H, H-8), 8.34 (dd, 1H, *J*=8.7, 1.7, H-4), 8.41 (s, 1H, H-10), 8.71 (s, 1H, H-9), 9.00 (dd, 1H, *J*=4.0, 1.7, H-2). *Anal.* Calcd for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.04; H, 5.18; N, 7.65.

Compound (**3**) was identified with commercial benzo[*f*]quinoline by the mixed melting point test. Ms: *m/z* 179 (M^+).

β-(5,6,7,8-Tetrahydro-2-naphthylamino)acrolein (4)

6-Aminotetralin (14.7 g, 0.1 mol) was treated with MDA as discribed for the preparation of **1**. The residue was recrystallized from acetone to give 16.8 g (92%) of **4** as colorless needles, mp 138-140 ℃. Ms: *m/z* 201 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 1.78 (m, 2H, H-6,7), 2.73 (m, 2H, H-5,8), 5.27 (d, 1H, *J*=7.4, H-11), 6.77 (d, 1H, *J*=2.0, H-1), 6.80 (dd, 1H, *J*=8.6, 2.0, H-3), 7.03 (dd, 1H, *J*=8.6, 2.0, H-4), 7.32 (d, 1H, *J*=7.4, H-10), 9.27 (dd, 1H, *J*=4.0, 2.0, CHO-12), 11.63 (br, d, 1H, *J*=8.0, NH-9). *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.35; H, 7.66; N, 7.04.

Cyclization of 4 with PPA

The same procedure was used as for the reaction of **2** with PPA using 2.01 g (0.01 mol) of **4**. The residue was confirmed to include 5,6,7,8-tetrahydro-1-azaanthracene (**5**, 42%) and 5,6,7,8-tetrahydro-1-azaphenanthrene (**6**, 23%) by the ^{1}H-nmr spectral analysis; because the separation of their products was very difficult.

5: ^{1}H-Nmr ($CDCl_3$): δ 1.70~2.00 (m, 4H, H-6,7), 2.60~3.10 (m, 4H, H-5,8), 7.26 (dd, 1H, *J*=8.1, 4.4, H-3), 7.48 (s, 1H, H-10), 7.80 (s, 1H, H-9), 8.02 (dd, 1H, *J*=8.1, 1.7, H-4), 8.79 (dd, 1H, *J*=4.4, 1.7, H-2).

6: ^{1}H-Nmr ($CDCl_3$): δ 1.70~2.00 (m, 4H, H-6,7), 2.60~3.10 (m, 4H, H-5,8), 7.38 (dd, 1H, *J*=8.4, 4.4, H-3), 7.42 (d, 1H, *J*=8.7, H-9), 7.85 (d, 1H, *J*=8.7, H-10), 8.28 (dd, 1H, *J*=8.4, 1.7, H-4), 8.85 (dd, 1H, *J*=4.4, 1.7, H-2).

N-Oxidation of 2

A solution of **2** (0.9 g, 5 mmol) and *m*-CPBA (1.3 g 7.5 mmol) in $CHCl_3$ (100 ml) was stirred at room temperature for 2 h. A solution of 5% Na_2CO_3 (100 ml) was added to the reaction mixture, and the whole was extracted with $CHCl_3$. The extract was dried over $MgSO_4$, the solution was evaporated off, and the residue was recrystallized from AcOEt to give 0.85 g (87%) of **7** as yellow needles, mp 144-146 ℃. Ms: *m/z* 195 (M^+), 179 (M^+-O). ^{1}H-Nmr ($CDCl_3$): δ 7.27 (d, 1H, *J*=8.7, 5.7, H-3), 7.61 (m, 2H, H-6,7), 7.94 (d, 1H, *J*=8.7, H-4), 8.04 (m, 1H, H-5), 8.15 (m, 1H, H-8), 8.47 (s, 1H, H-10), 8.63 (d, 1H, *J*=5.7, H-2), 9.35 (s, 1H, H-9). *Anal.* Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.79;

H, 4.65; N, 7.19.

Reissert Reaction of 2

Compound (**2**) (0.9 g, 5 mmol), trimethylsilyl cyanide (0.75 g, 7.5 mmol) and anhydrous $AlCl_3$ (5 mg) were stirred under nitrogen atmosphere in dry CH_2Cl_2 (20 ml). After 2 min, acetyl chloride 0.6 g (7.5 mmol) (or benzoyl chloride 1.05 g, 7.5 mmol) was added and the mixture was stirred at room temperature for 24 h. The reaction mixture was washed, successively with two 20 ml portions of H_2O, 5% HCl, H_2O, 5% NaOH, and finally with H_2O, dried over $MgSO_4$. The solvent was evaporated and the residue was recrystallized from AcOEt to give 1-acetyl- (or 1-benzoyl-) 1,2-dihydrobenzo[*g*]quinoline-2-carbonitril (**8**) (or **9**).

8: 0.84 g (68%), pale yellow gummy. Ms: *m/z* 248 (M^+), 205 (M^+-$COCH_3$), 179 (205-CN). ^{1}H-Nmr ($CDCl_3$): δ 2.33 (s, 3H, CH_3), 6.17 (dd, 1H, *J*=9.1, 6.1, H-3), 6.55 (d, 1H, *J*=6.1, H-2), 6.93 (d, 1H, *J*=9.1, H-4), 7.53 (m, 2H, H-6,7), 7.65 (s, 1H, H-10), 7.71 (s, 1H, H-9), 7.83 (m, 2H, H-5,8). *Anal.* Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.32; H, 4.86; N, 11.04.

9: 0.96 g (62%), colorless needles, mp 207-208 ℃. Ms: *m/z* 310 (M^+), 205 (M^+-COPh), 179 (205-CN). ^{1}H-Nmr (DMSO-d_6): δ 6.35 (d, 1H, *J*=6.1, H-2), 6.41 (dd, 1H, *J*=8.7, 6.1, H-3), 7.12 (s, 1H, H-9), 7.20 (d, 1H, *J*=8.7, H-4), 7.28～7.48 (m, 8H, H-6～8, H-arom), 7.88 (m, 1H, H-5), 7.94 (s, 1H, H-10). *Anal.* Calcd for $C_{21}H_{14}N_2O$: C, 81.27; H, 4.55; N, 9.03. Found: C, 81.05; H, 4.47; N, 8.86.

1-Benzoyl-1,2-dihydrobenzo[*g*]quinoline-2-phosphonate (10)

A mixture of **2**, (0.9 g, 5 mmol) and dry CH_3CN (30 ml) was chilled to 0-5 ℃, and benzoyl chloride (1.4 g, 10 mmol) was added. After the solution was stirred for 20 min, trimethyl phosphite (1.24 g, 10 mmol) and NaI (2.25 g, 15 mmol) were added successively at 0 ℃. The mixture was stirred at 50 ℃ for 20 min. After cooling, 5% $NaHCO_3$ (10 ml) was added and the aqueous solution was extracted with CH_2Cl_2 (2 X 30 ml). The extract was dried over $MgSO_4$ and evaporated, and the residue was recrystallized from AcOEt to give 1.26 g (64%) of **10**, as colorless needles, mp 238-240 ℃. Ms: *m/z* 393 (M^+), 288 (M^+-COPh). ^{1}H-Nmr ($CDCl_3$): δ 3.52 (d, 3H, *J*=10.8, $POCH_3$), 3.73 (d, 3H, *J*=10.8, $POCH_3$), 5.98 (dd, 1H, *J*=20.8, 6.1, H-2), 6.33 (m, 1H, H-3), 6.90 (m, 1H, H-4), 6.91 (s, 1H, H-9), 7.15～7.56 (m, 6H, H-6～8, H-arom), 7.72 (m, 1H, H-5), 7.57 (s, 1H, H-10), 8.08 (m, 2H, H-arom). *Anal.* Calcd for $C_{22}H_{20}NO_4P$: C, 67.17; H, 5.12; N, 3.56. Found: C, 67.33; H, 5.08; N, 3.42.

Reaction of 2 with Methylsulfinylmethyl Carbanion (Methylation)

To a solution of 1.44 g (30 mmol) of 50% NaH in 100 ml of Me_2SO at 70 ℃ was added 0.9 g (5 mmol) of

2 in 100 ml of Me_2SO. The reaction mixture was stirred for 1 h at 70 ℃ under a nitrogen atmosphere followed by the addition of 100 ml of water. The reaction mixture was neutralized with aqueus 10% HCl which was extracted with four 100 ml portions of $CHCl_3$. The combined $CHCl_3$ extracts were washed with tree 100 ml portions of water, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel ($CHCl_3$) to give products (**11-14**) (Table 2). The structure of **11-14** were confirmed by their ^{1}H-nmr spectra and the structure of **12** was confirmed by the nOe mesurement.

11: mp 63-65 ℃. Ms: *m/z* 193 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 2.84 (s, 3H, CH_3-4), 7.22 (d, 1H, *J*=4.0, H-3), 7.53 (m, 2H, H-6,7), 8.07 (m, 2H, H-5,8), 8.55 (s, 1H, H-10), 8.70 (s, 1H, H-9), 8.85 (d, 1H, *J*=4.0, H-2). *Anal*. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.87; H, 5.86; N, 7.22.

12: mp 129-130 ℃. Ms: *m/z* 207 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 2.83 (s, 3H, CH_3-4), 3.30 (s, 3H, CH_3-9), 7.22 (d, 1H, *J*=4.0, H-3), 7.55 (m, 2H, H-6,7), 8.06 (m, 1H, H-5), 8.33 (m, 1H, H-8), 8.43 (s, 1H, H-10), 8.89 (d, 1H, *J*=4.0, H-2). NOe: irradiation at δ 2.83 (CH_3-4)--2.7% and 4.5% enhancement at δ 7.22 (H-3) and 8.43 (H-10); irradiation at δ 8.06 (H-5)--8.2% and 9.2% enhancement at δ 7.55 (H-6) and 8.43 (H-10); irradiation at δ 8.43 (H-10)--9.0% and 8.9% enhancement at δ 2.83 (CH_3-4) and 8.06 (H-5). *Anal.* Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.75; H, 6.24; N, 6.51.

13: mp 93-94 ℃. Ms: *m/z* 207 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 2.73 (s, 3H, CH_3-4), 2.80 (s, 3H, CH_3-2), 7.13 (s, 1H, H-3), 7.50 (m, 2H, H-6,7), 8.05 (m, 2H, H-5,8), 8.50 (s, 1H, H-10), 8.60 (s, 1H, H-9). *Anal.* Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.85; H, 6.57; N, 6.89.

14: mp 123-125 ℃. Ms: *m/z* 221 (M^+). ^{1}H-Nmr ($CDCl_3$): δ 2.76 (s, 3H, CH_3-4), 2.78 (s, 3H, CH_3-2), 3.28 (s, 3H, CH_3-9), 7.12 (s, 1H, H-3), 7.53 (m, 2H, H-6,7), 8.03 (m, 1H, H-5), 8.30 (m, 1H, H-8), 8.38 (s, 1H, H-10). *Anal.* Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.97; H, 6.64; N, 6.30.

Reaction of 7 with Methylsulfinylmethyl Carbanion

The same procedure was used as for the reaction of **2** with methylsulfinylmethyl carbanion using 0.98 g (5 mmol) of **7**. The residue was chromatographed on silica gel (CH_2Cl_2:Me_2CO = 20:1) to give 0.44 g (42%) of **15** as yellow needles (from AcOEt), mp 123-125 ℃. Ms: *m/z* 209 (M^+), 193 (M^+-O). ^{1}H-Nmr ($CDCl_3$): δ 2.77 (s, 3H, CH_3-2), 7.25 (d, 1H, *J*=8.7, H-3), 7.57 (m, 2H, H-6,7), 7.79 (d, 1H, *J*=8.7, H-4), 8.01 (m, 1H, H-5), 8.12 (m, 1H, H-8), 8.38 (s, 1H, H-10), 9.32 (s, 1H, H-9). *Anal.* Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.53; H, 5.37; N, 6.80.

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